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AN INVESTIGATION OF LIGHT-CATALYZED CHLORINE OXIDATION FOR TREATMENT OF WASTEWATER

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AN INVESTIGATION OF LIGHT-CATALYZED CHLORINE OXIDATION FOR TREATMENT OF WASTEWATER

by

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The Advanced Waste Treatment Research Laboratory
Robert A. Taft Water Research Center

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FOREWORD

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ABSTRACT

A study was made of the effect of ultraviolet radiation on the rate and extent of chlorine oxidation of organic material in highly nitrified effluents from biological sewage treatment plants. Ultraviolet radiation will very significantly increase the rate of this reaction. Also, the extent of oxidation which can be achieved by chlorine combined with UV radiation is usually much greater than that which can be achieved by chlorine alone.

The rate of the catalytic oxidation is dependent upon pH, and the most rapid rate of oxidation and most efficient use of chlorine are obtained at pH 5. In seven different experiments performed at pH 5, the average COD decrease was 67% in 5 min., 79% in 10 min. and 95% in 15 min.

The rate of organic oxidation is not proportional to the chlorine concentration; however, the rate of chlorine consumption is. Large excesses of chlorine do not increase the reaction rate but simply increase the amount of chlorine required to eliminate a given amount of organic matter.

The rate and extent of the catalytic organic oxidation at pH 5 are not significantly affected by temperature. However, both the rate and extent of catalytic oxidation are substantially reduced by the presence of ammonia in an effluent.

A brief investigation of the scope of the UV-catalyzed chlorine oxidation indicated that phenol, 2,4-dinitrophenol, glycine, formic acid, and _o_-dinitrobenzene are oxidized rapidly and extensively.

On the basis of organic oxidation rate produced per watt of UV output, high-pressure mercury arcs are about 2.7 times more efficient than low-pressure mercury arcs.

Process costs of 7.2¢ to 11.1¢/1000 gal. were estimated, based on several types of commercially available lamps.

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SUMMARY

WASTEWATER OXIDATION STUDIES - THE EFFECTS OF pH AND IRRADIATION TIME

Ultraviolet radiation will very significantly increase the rate at which chlorine will oxidize the organic material in highly nitrified wastewater. Also, the extent of oxidation which can be achieved by chlorine and UV radiation is usually much greater than that which can be achieved by chlorine alone; 5 to 8 times more TOC and COD could be eliminated in 10 min. by chlorine plus UV radiation than could be eliminated in 6 days by chlorine in the dark.

The rate of the catalytic organic oxidation is dependent upon pH, and the most rapid rate of oxidation and most efficient use of chlorine are obtained at pH 5. The rate of organic oxidation at pH 6.5 is not as fast as at pH 5, but is faster than at pH 8.5. The organic oxidation rate is much slower at pH 3 and at pH 10.

Ultraviolet radiation alone will produce reduction in the COD and TOC of an effluent; however, UV radiation plus chlorine is 3 to 10 times faster, depending upon pH; at pH 5, COD is eliminated more than 8 times faster, and TOC is eliminated 4.5 times faster.

The wastewaters examined contained variable quantities of readily oxidizable organic material. The chemical oxygen demand (COD) which could be eliminated within 10 min. by chlorine in the dark averaged 12% (range 0.8-20%). The extent of total organic carbon (TOC) elimination during this time averaged 6% (range 0-15%).

The oxidations of four different effluents were investigated at pH 5. In seven different experiments, the average COD decrease was 67% in 5 min. (range 51-84%), 79% in 10 min. (range 66-100%), and 95% in 15 min. (range 88-100%). The average TOC decrease was 33% in 5 min. (range 15-50%), 52% in 10 min. (range 44-60%), and 75% in 15 min. (range 70-81%).

The rate of COD elimination at pH 5 is most rapid during the first 5 min. and decreases as the oxidation proceeds. The rate of TOC elimination, however, is nearly linear over a 15-min. period.

Effect of Chlorine Concentration

The rate of COD and TOC elimination is not proportional to the chlorine concentration; however, the rate of chlorine consumption is. Large excesses of chlorine do not increase the reaction rate but simply increase the amount of chlorine required to eliminate a given amount of organic matter. Most efficient use of chlorine is obtained when the chlorine is added gradually during the irradiation period.

Effect of Temperature

The rate and extent of the catalytic organic oxidation at pH 5 are not significantly affected by temperature. The rate of COD elimination at 25°C (77°F) is only slightly greater than it is at 5°C (41°F). The rates of TOC elimination are about the same at both temperatures.

Effect of Ammonia

The presence of ammonia in an effluent drastically reduces the rate and extent of the UV-catalyzed chlorine oxidation of organic matter. For example, the addition of 23 ppm of ammonia nitrogen to a highly nitrified effluent reduces the organic oxidation rate by more than tenfold. The amount of chlorine actually required to eliminate 1 ppm of ammonia is about four times the theoretical amount required to eliminate 1 ppm of COD. Also, the oxidation of organic matter is greatly inhibited until all the ammonia is oxidized.

In water, ammonia reacts with chlorine to form mono-, di- and trichloramine in various proportions, depending upon pH and ratio of reactants. At pH 5, an excess of chlorine rapidly converts most of the ammonia to trichloramine which is relatively stable in the presence of excess chlorine. Irradiation of an ammonia-chlorine reaction mixture rapidly accelerates the conversion of trichloramine to nitrate and other oxidation products of ammonia including, presumably, nitrogen gas.

Oxidation of Pure Compounds

A brief investigation was made of the effect of UV-catalyzed chlorine oxidation on the TOC of water containing eight pure organic compounds. The following compounds are oxidized rapidly and extensively: phenol (61%, 8 min.), 2,4-dinitrophenol (53%, 10 min.), glycine (61%, 4 min.), formic acid (90%, 4 min.), and o-dinitrobenzene (65%, 10 min.). Benzoic acid is also oxidized (45%, 10 min.), but not as fast as the other compounds. Acetic acid and ethanol are oxidized at a much slower rate (less than 10%, 10 min.).

Other Oxidizing Agents

A very brief study was made of the extent of organic oxidation produced when wastewater was treated with UV radiation plus (1) molecular oxygen and (2) hydrogen peroxide. No significant decrease in TOC was detected after oxygen had been bubbled through an irradiated reaction mixture for 20 min. Hydrogen peroxide produced no significant decrease in TOC after 30 min. in the dark; irradiation of this reaction mixture for another 30 min. produced only a slight decrease in TOC.

Ultraviolet Sources

At the present time, mercury-arc lamps are probably the most practical sources of UV radiation for the catalytic chlorine oxidation of organic material in wastewater. On the basis of organic oxidation rate produced per watt of UV output, high-pressure mercury arcs, which emit a broad spectrum of wavelengths (220 - 366 mμ), are about 2.7 times more efficient than low-pressure mercury arcs which emit almost exclusively at one wavelength (253.7 mμ).

Process Costs

Process cost estimates were made for large-scale application of UV-catalyzed chlorine oxidation to wastewater. Costs of 7.2¢ to 11.1¢/1000 gal. were estimated employing commercially available UV lamps. The assumptions made were that a contact time of 10 min. is required for effective organic oxidation and that the catalytic process requires the application of 15 times more radiant energy than that required for UV sterilization.

Process costs could be lowered substantially if any one of the following factors could be reduced: (1) the amount of radiant energy per unit volume required for effective oxidation, (2) the contact time and (3) the cost of the radiation source. The precise determination of these factors will require a study designed to determine exactly how much wastewater can be treated effectively using each radiant energy source.

INTRODUCTION

Earlier studies at Midwest Research Institute had demonstrated that ultraviolet radiation strongly accelerates the rate at which aqueous chlorine oxidizes starch and other organic compounds.[1,2] Chlorine is widely used for the disinfection of water. However, in the absence of ultraviolet radiation, chlorine will oxidize only a small fraction of the organic material in wastewater.[3,4]

The purpose of the present work was to determine the usefulness of ultraviolet-catalyzed chlorine oxidation in producing more extensive, and more rapid, removal of the organic material in highly nitrified wastewater. Another objective was to estimate the cost of large-scale application of this process. The results of this research are presented in nine major sections.

The first series of wastewater oxidation experiments was a general investigation of the effect of pH, and a comparison of the rate and extent of organic oxidation which could be achieved by chlorine plus UV radiation, by chlorine alone, and by UV radiation alone.

The second series of wastewater oxidation experiments was designed to determine the effect of variation in the amount of chlorine applied, variation in irradiation time, and the effect of relatively small differences in pH.

The third series of wastewater oxidation experiments was designed to clarify further the effects of pH and chlorine concentration, and to determine whether or not the catalytic oxidation was subject to a temperature effect.

The fourth section discusses the problems which arise if relatively large amounts of ammonia (15-30 ppm) are present in the effluent.

The fifth section discusses the results of a direct investigation of the ammonia-chlorine reaction.

The relative effectiveness of two major types of UV sources is discussed in a sixth section.

The various factors which influence the cost of large-scale application of this process are discussed in a seventh section.

The eighth section describes briefly the application of UV-catalyzed chlorine oxidation to pure organic compounds.

The final section discusses the effect of UV radiation on the oxidizing action of oxygen and hydrogen peroxide.

FIRST SERIES OF WASTEWATER OXIDATION EXPERIMENTS

Summary

Experiments in this series showed that the oxidation of organic matter in wastewater by chlorine is much faster when the reaction mixture is irradiated than when the reaction mixture is kept in the dark. The extent of COD elimination in the catalytic process is always greater than the extent of TOC elimination.

Chlorine plus UV radiation produces organic oxidation 3 to 10 times faster than UV radiation alone, depending upon pH.

Considerable portions of ammonia in wastewater are converted to nitrate by the UV-catalyzed chlorine oxidation process.

First Series of Wastewater Oxidation Experiments

The first series of experiments was designed to compare (1) the effects of two pH levels (pH 5 and pH 10), (2) the difference between reaction in the dark and reaction when irradiated, and (3) the difference between radiation alone and radiation plus chlorine. The design of this series of experiments is shown in Table I.

TABLE I

EXPERIMENTAL DESIGN,
FIRST SERIES OF EXPERIMENTS

	Experiment Number	
	pH 5	pH 10
Chlorine, plus irradiation	3	4
Irradiation, no chlorine	5	6
Chlorine, no irradiation	7	8

The pH levels of 5 and 10 were chosen because, at pH 5, the active chlorine in solution is 100% hypochlorous acid; while, at pH 10, the active chlorine is 100% hypochlorite[5/] (Figure 1).* These two reagents would be expected to react differently in the catalyzed oxidation because of their distinctly different ultraviolet spectra (Figure 2).

The procedures used in this series were slightly different from those used subsequently. The effluent in this series was acidified at the point of collection (4 ml. H_2SO_4/gal), and the pH was adjusted prior to each experiment using 40% sodium hydroxide. In subsequent experiments, acidification at the point of collection was omitted. Also, contrary to subsequent procedures, the UV lamp in this series was not allowed to reach maximum irradiation intensity before being inserted into the reactor.

The analytical results obtained for chlorine concentration, COD and TOC (which are presented in Figures 3-8) are summarized in Tables II and III.

The first conclusion derived from this series of exploratory experiments is that the oxidation proceeds many times faster upon irradiation than it does in the dark. Thus, the indicated rate of oxidation at pH 5, as measured by the rate of TOC elimination and the rate of chlorine consumption, is 60 to 100 times faster upon irradiation than it is in the dark.

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* Figures in this report are inserted at the end of the section to which they apply.

TABLE II

RATES OF DECREASE IN CHLORINE CONCENTRATION, TOC AND COD IN FIRST SERIES OF EXPERIMENTS

	Reaction Conditions			Average Rate of Decrease in Chlorine Concn.	Average Rate of TOC Decrease	Average Rate of COD Decrease
Exp. No.	Initial Cl_2 Concn. (ppm)	pH	Types of Irrad.	(ppm/min)	(ppm/min)	(ppm/min)
3	150	5	UV	8.82	0.237	1.08
4	150	10	UV	6-22[a]	0.22	1.10
5	0	5	UV	--	0.051	0.132
6	0	10	UV	--	0.073	0.110
7	150	5	None	0.133[b]	0.0037	--
				0.055[b]	--	0.012
8	150	10	None	0.290[b]	0.016	--
				0.0177[b]	0.00066	0.00033

---

[a] In this experiment the chlorine disappearance was very rapid, so that this value could only be estimated.

[b] In Experiments 7 and 8, the chlorine concentration apparently decreased at a non-linear rate (see Figures 7 and 8) until it reached a certain level (about 65 ppm); then it remained constant. The first values refer to rates during the first few hours of the experiment. The second values were calculated for the duration of the entire experiment (1,340 min. for Experiment 7; 4,535 min. for Experiment 8).

TABLE III

EXTENT OF COD AND TOC DECREASE IN FIRST SERIES OF EXPERIMENTS

	Reaction Conditions			COD Decrease		TOC Decrease	
Exp. No.	Initial Cl_2 Concn. (ppm)	pH	Types of Irrad.	(%)	(min.)[a]	(%)	(min.)[a]
3	150	5	UV	95	27	55	27
4	150	10	UV	82	20	25	20
5	0	5	UV	82	170	73	170
6	0	10	UV	59	145	84	145
7	150	5	None	51	1,341	12	1,341
8	150	10	None	16	4,535	15	4,353

---

[a] Irradiation time or reaction time depending on the nature of the experiment.

However, these differences in reaction rates are somewhat exaggerated because the rate of oxidation in the dark is most rapid at the beginning of the oxidation; and, in these experiments, the oxidation in the dark was essentially complete long before the final COD and TOC samples were taken. The gradual slowing of the oxidation rate in the dark is indicated from the plot of chlorine consumption vs. time in Experiment 7 (Figure 7). Subsequent studies (see the later section entitled "Second Series of Experiments") have shown that there is wide variation in the amount of organic material which can be oxidized in 10 min. in the dark. However, when irradiation is begun after 10 min. in the dark, the rate of organic oxidation is increased up to 15-fold.

The second general conclusion drawn from this series of experiments was that the extent of COD elimination is significantly greater than the extent of TOC elimination. This conclusion was shown to be valid for all subsequent experiments.

In the initial series of experiments, there appeared to be little difference between pH 5 and pH 10 in respect to the rate of TOC and COD elimination. However, this similarity was the result of inopportune sampling times (see Figures 3 and 4), and subsequent experiments indicated that the rate of organic oxidation is considerably greater at pH 5 than at pH 10.

A third conclusion from this series of experiments was that chlorine plus UV radiation produces more rapid decreases in TOC and COD than UV radiation alone. Comparing rates produced by chlorine plus UV radiation at pH 5 with rates produced by UV radiation alone at pH 5, COD is eliminated 8.2 times faster, and TOC is eliminated 4.5 times faster; at pH 10, COD is eliminated 10 times faster, and TOC is eliminated 3 times faster. Subsequent experiments (see "Second Series of Experiments", p. 18) indicated that, at pH 6.5, chlorine plus UV radiation eliminates COD about 7 times faster than radiation alone.

The effluent used in this first series contained considerable amounts of ammonia (2-6 ppm N). Some difficulties in precision were encountered in these ammonia determinations because of turbidity, which was probably the result of required adjustments in pH. Ammonia concentrations determined for the first series of experiments are shown in Table IV. In every experiment in which chlorine was present, there were very significant decreases in ammonia concentration. (The ammonia-chlorine reaction is examined in greater detail in the section concerning the oxidation of high-ammonia effluents, p. 49, and the section concerning the ammonia-chlorine reaction, p. 54).

Ultraviolet radiation alone (Experiments 5 and 6) had almost no effect on ammonia concentration. This conclusion was verified in a subsequent experiment (Experiment 15, p. 115).

TABLE IV

AMMONIA CONCENTRATIONS
(First Series of Experiments)

Exp. No.	Reaction Conditions Initial Cl_2 Concn. (ppm)	pH	Types of Irrad.	Reaction Time (min.)	Ammonia (ppm N) Initial	Final
3	150	5	UV	27	4.0	2.1
4	150	10	UV	20	2.1	2.8
5	0	5	UV	171	6.4[a]	7.2
6	0	10	UV	145	6.4[a]	6.6
7	150	5	None	1,341	4.8[b]	2.7
8	150	10	None	21	5.3[b]	2.9
				4,535		2.3

---

[a] These ammonia values were obtained using a relatively fresh sample of effluent.

[b] Considerable turbidity was noticed in these samples.

In this first series of experiments, the observation was made that significant quantities of ammonia were oxidized to nitrate in the experiments in which the effluent was exposed to UV radiation and chlorine (Experiments 3 and 4); there were substantial increases in nitrate concentration (Table V). Chlorine in the dark also produced an increase in nitrate concentration (Experiments 7 and 8), but this increase was not as great as that produced by chlorine plus irradiation. UV radiation alone actually decreased the nitrate concentration. This observation was confirmed in Experiment 15, p. 115. The formation of nitrate in the ammonia-chlorine reaction was investigated further in subsequent experiments (see the two sections of this report concerned with the oxidation of high-ammonia effluents, p. 49, and the section concerned with the ammonia-chlorine reaction, p. 54).

TABLE V

NITRATE CONCENTRATIONS
(First Series of Experiments)

Exp. No.	Reaction Conditions Initial Cl_2 Concn. (ppm)	pH	Types of Irrad.	Reaction Time (min.)	Nitrate (ppm N) Initial	Final
3	150	5	UV	27	0.50	2.44
4	150	10	UV	20	--	2.85
5	0	5	UV	196	0.50	0.20
6	0	10	UV	145	--	0.09
7	150	5	None	1,341	0.26	1.95
8	150	10	None	4,535	--	1.27

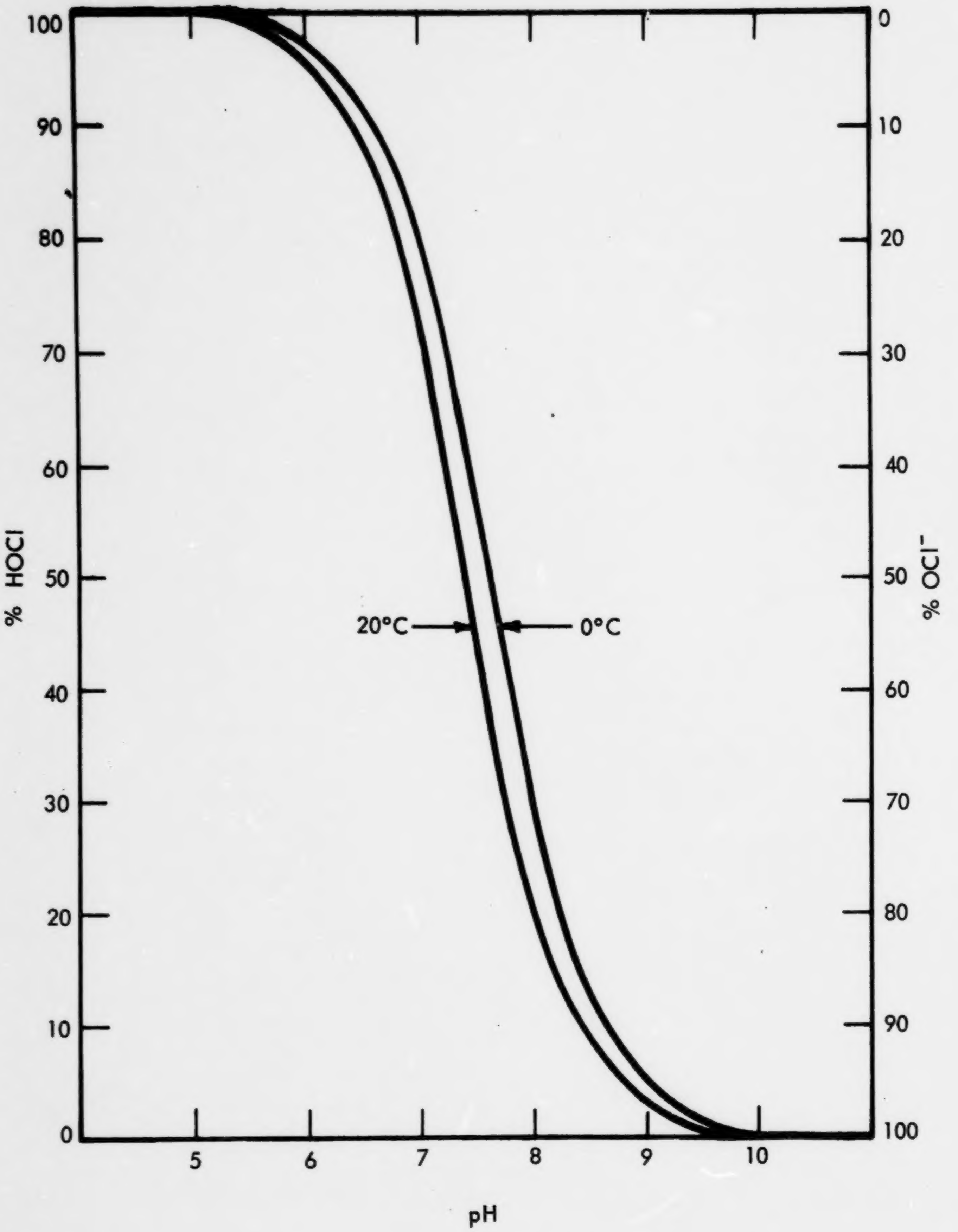

Figure 1 - Relative Amounts of HOCl and OCl$^-$ at Various pH Levels

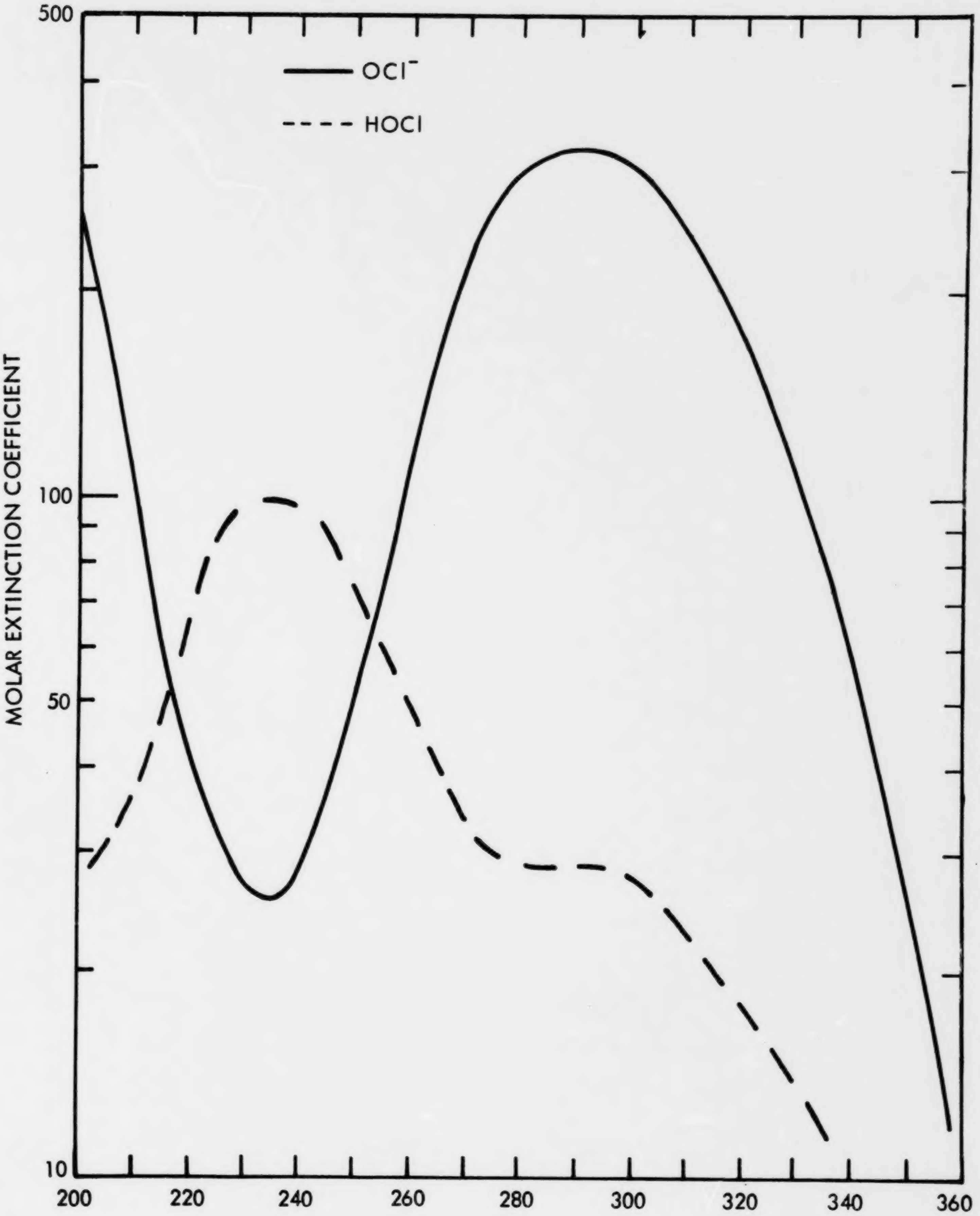

Figure 2 - Ultraviolet Spectra of Hypochlorous Acid and Hypochlorite Ion

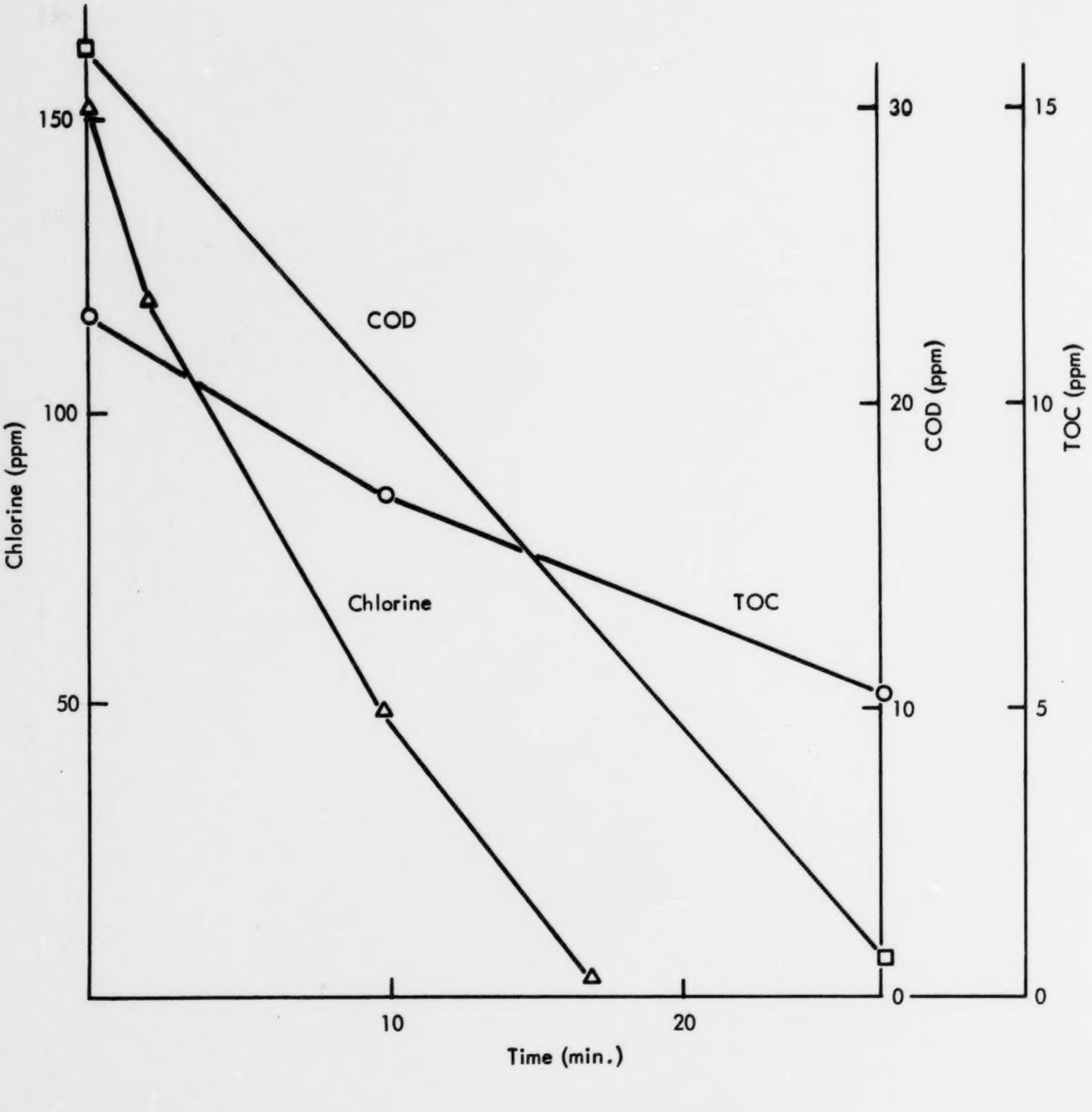

Figure 3 - UV-Catalyzed Chlorine Oxidation of Effluent G-1 at pH 5 (Experiment 3)

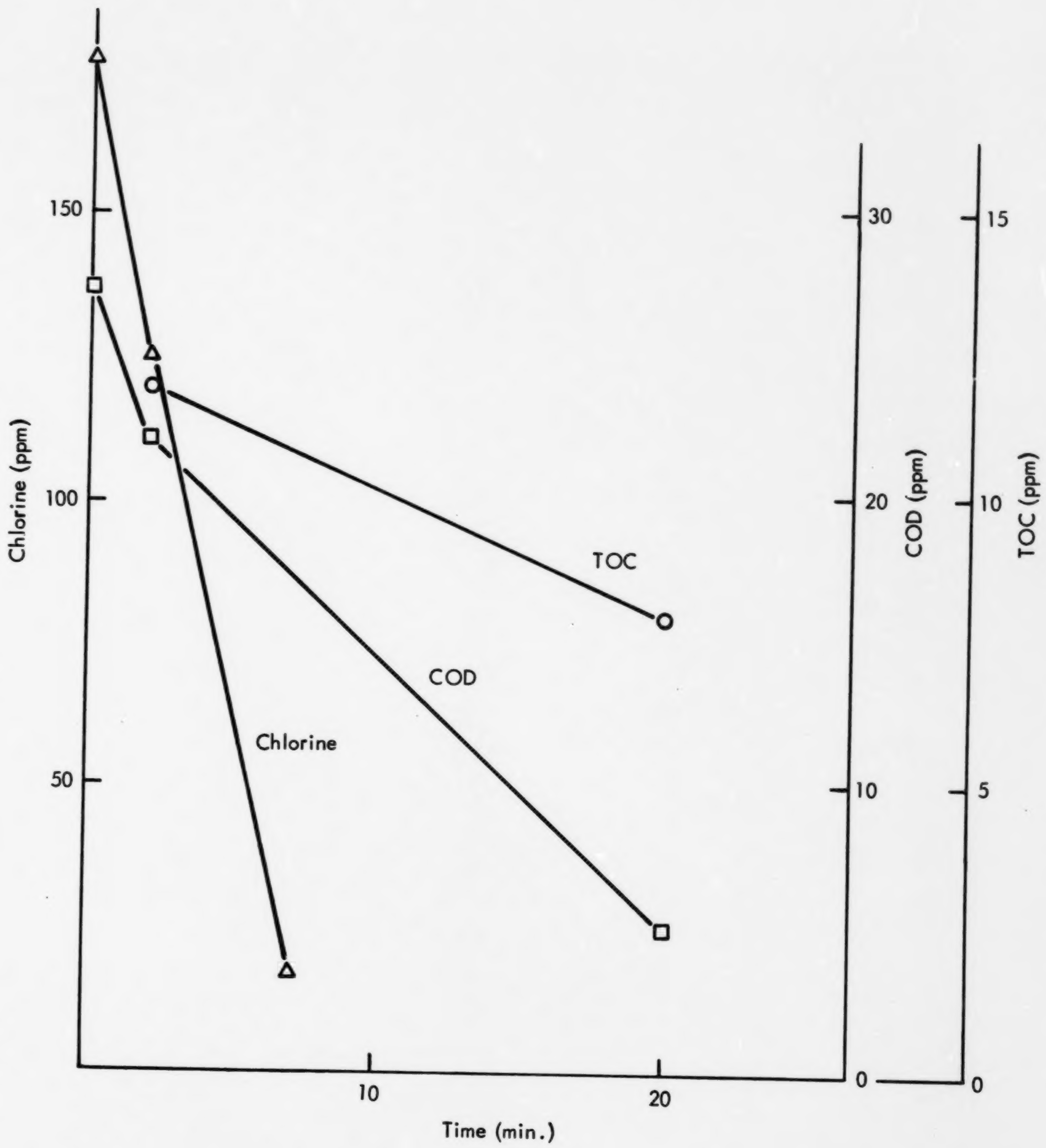

Figure 4 - UV-Catalyzed Chlorine Oxidation of Effluent G-1 at pH 10 (Experiment 4)

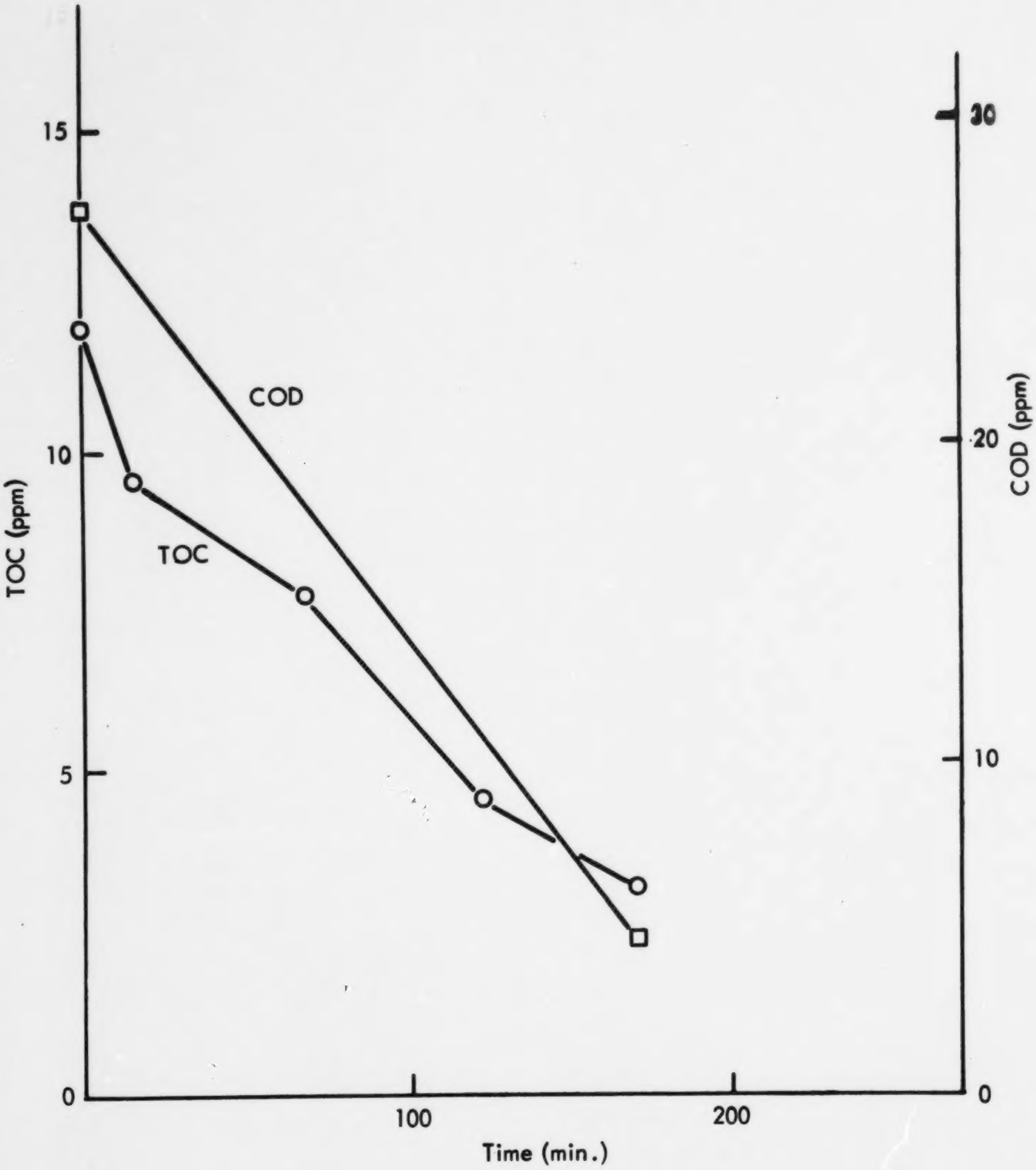

Figure 5 - Ultraviolet Irradiation of Effluent G-1 at pH 5 (Experiment 5)

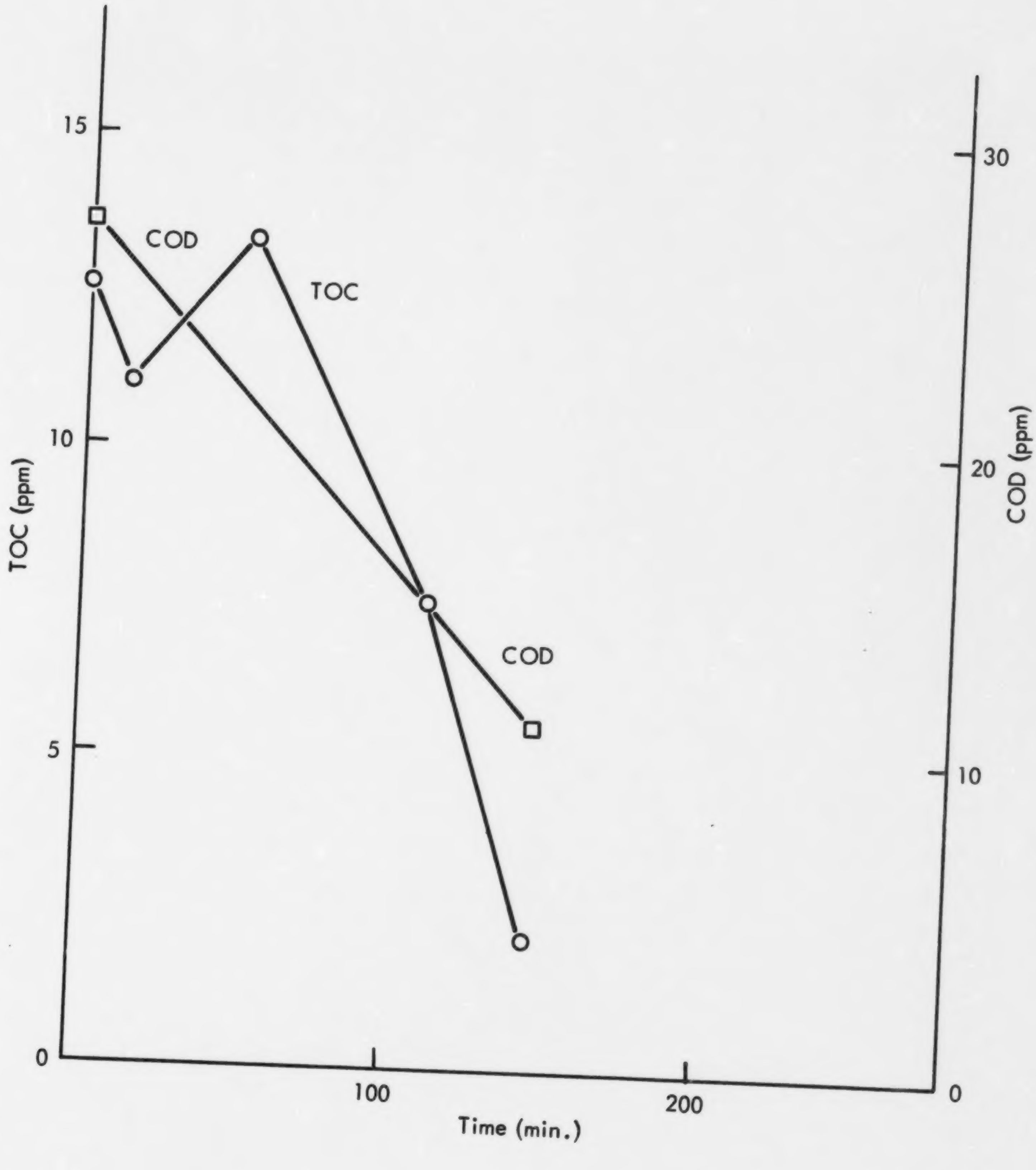

Figure 6 - Ultraviolet Irradiation of Effluent G-1 at pH 10 (Experiment 6)

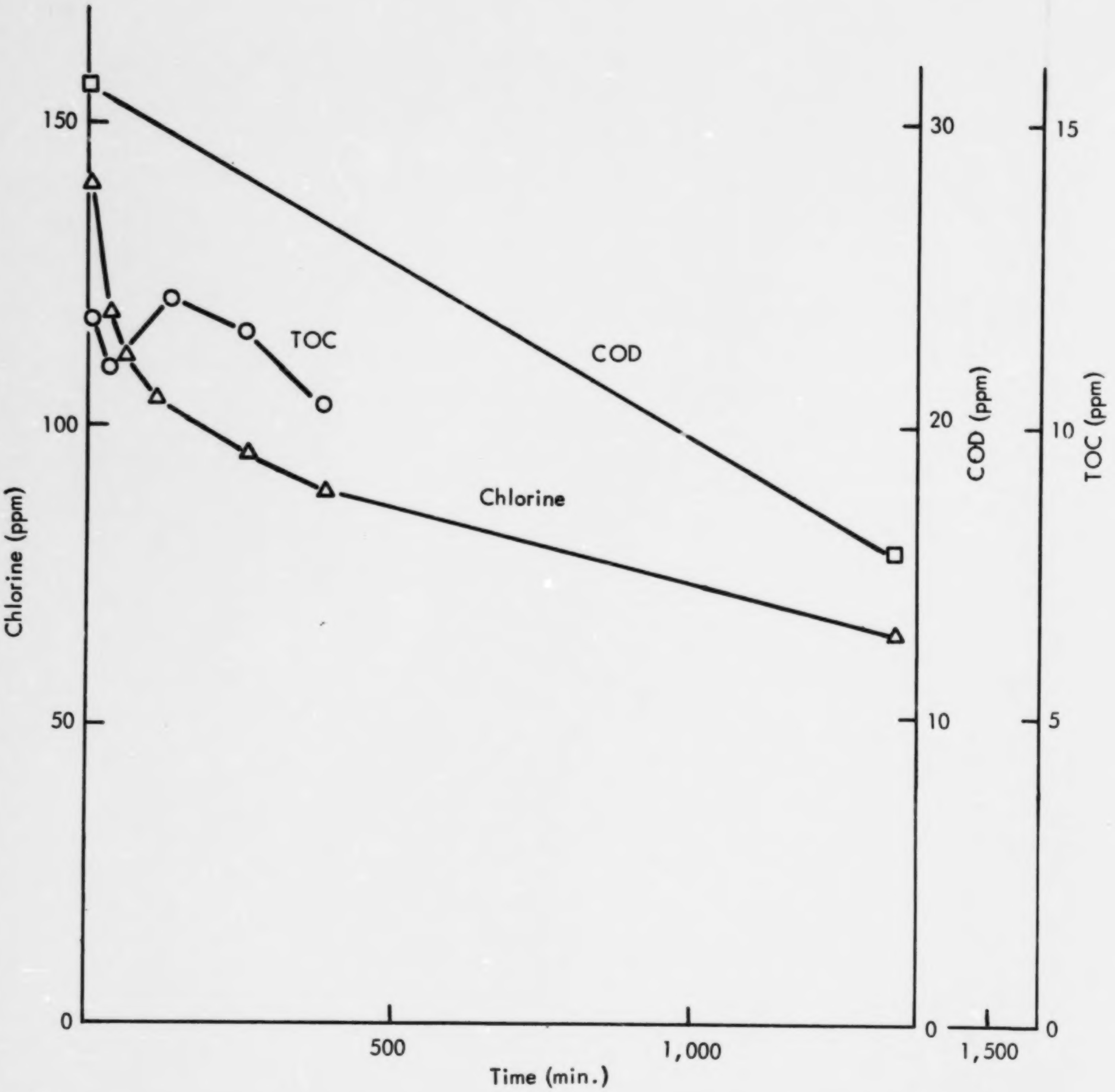

Figure 7 - Chlorination of Effluent G-1 at pH 5 (Experiment 7)

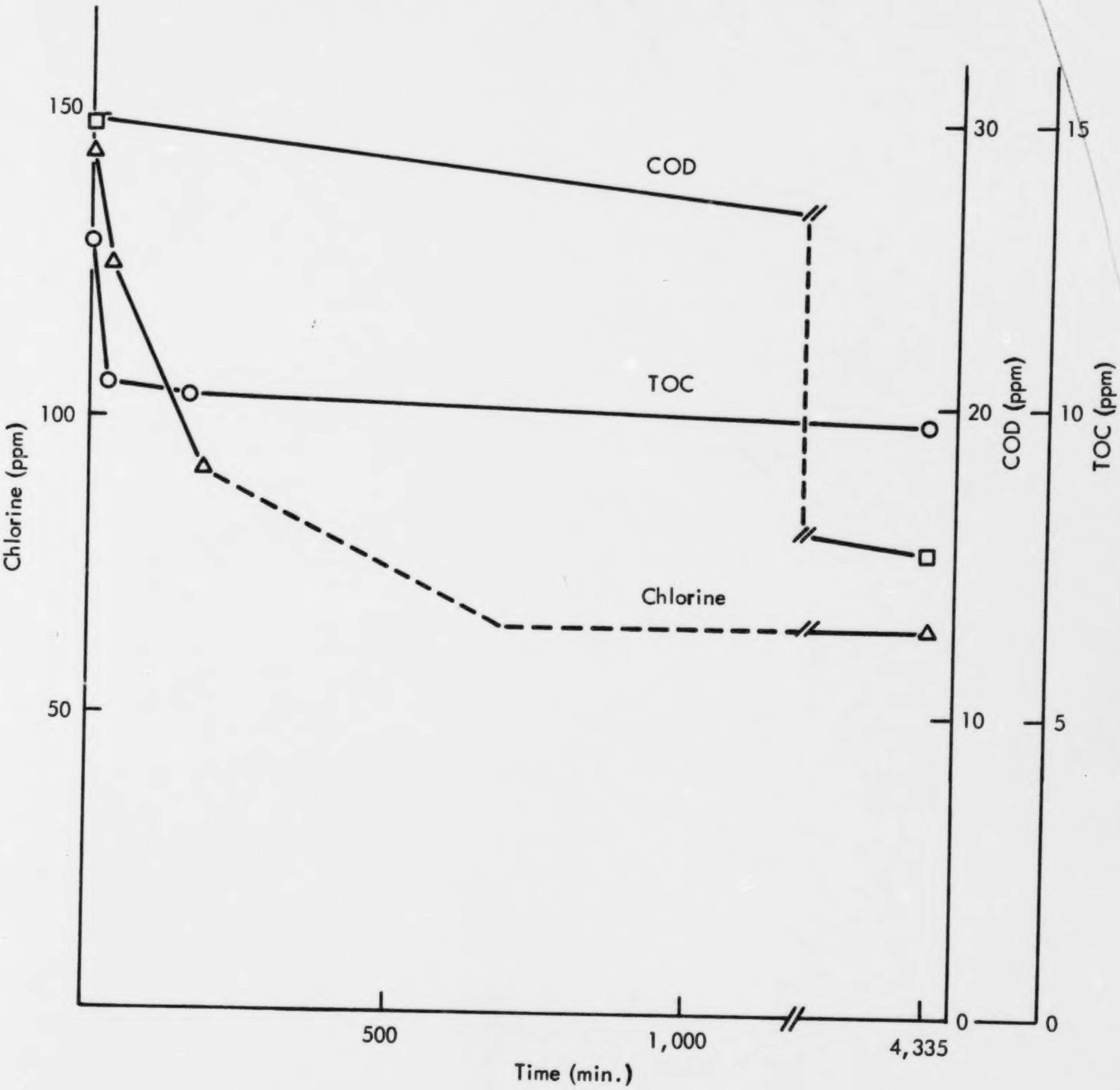

Figure 8 - Chlorination of Effluent G-1 at pH 10 (Experiment 8)

SECOND SERIES OF WASTEWATER OXIDATION EXPERIMENTS

Summary

Experiments performed in this series indicated that, in the UV-catalyzed process, the extent of organic oxidation is proportional to the irradiation time, but not to chlorine concentration. The catalytic oxidation rate is faster at pH 6.5 than at pH 8.5; the average extent of COD decrease produced in 10 min. was 60.0% at pH 6.5 and 45.6% at pH 8.5. (The organic oxidation rate is fastest at pH 5, and experiments performed at pH 5 are described in the third series of wastewater oxidation experiments.)

Experiments performed in this series and in the third series have indicated that considerable variation exists in the amount of organic oxidation which can be achieved when wastewater samples are treated for 10 min. with chlorine in the dark. In 13 experiments employing six different effluents, the extent of COD elimination during 10 min. in the dark averaged 12% (range 0.8-20%) and the extent of TOC elimination during this time averaged 6% (range 0-15.3%).

Second Series of Wastewater Oxidation Experiments

The low-ammonia effluents used in the second series of experiments were obtained from two sources. First, a laboratory-scale activated sludge apparatus was constructed and used to reduce the ammonia content of high-ammonia municipal effluents. (This apparatus is described in the Experimental Section.) Second, a reliable source of the desired type of highly nitrified effluent was located. This source was a sewage treatment plant of the activated sludge, extended aeration type. The plant was of novel design and was operated on an experimental basis by the Smith and Loveless Corporation.

Our experimental work continued using effluents obtained from both of these sources.

A series of nine, effluent, oxidation experiments was designed to investigate simultaneously the effect on COD and TOC of two levels, each, of chlorine concentration, irradiation time and pH.

The chlorine concentrations investigated consisted of (1) a slight excess over the theoretical amount of chlorine, and (2) a large (75%) excess over the theoretical value.

Irradiation times of 10 and 15 min. were examined to determine whether or not significant differences in COD and TOC elimination are caused by differences in irradiation time of this magnitude. In these experiments the UV lamp was allowed to warm up and was emitting maximum-intensity radiation when inserted into the reactor.

The pH levels of 6.5 and 8.5 were selected for study. These values are only about 1 pH unit different from the pH of the untreated effluent, but variations of this magnitude could have a large effect on the oxidation reaction; at pH 6.5 about 90% of the available chlorine is present as undissociated hypochlorous acid and, at pH 8.5, about 90% of the available chlorine exists as hypochlorite ion (see Figure 1).

A complete factorial experiment was designed, and the order of experiments was randomized. The design and randomization of the experiments are shown in Table VI. The numbers refer to actual experiment numbers; that is, Experiment 39 was run first, and Experiment 47 was run last in this series.

In Experiment 41, no chlorine was used, no pH adjustment was made, and the effluent was exposed to UV radiation for 10 and 15 min.

TABLE VI

EXPERIMENTAL DESIGN
(Experiments 39 - 47)

	pH 6.5		pH 8.5	
	High Cl_2 (175 ppm)	Low Cl_2 (102 ppm)	High Cl_2 (175 ppm)	Low Cl_2 (102 ppm)
Short irradiation time (10 min.)	43[a]	46	47	40
Long irradiation time (15 min.)	44	45	39	42

---

a/ The numbers 39-47 refer to experiment numbers. The experiments were performed in random order and are numbered in the order in which they were performed.

The effluent (S&L-5) used in these experiments was obtained from the Smith and Loveless, experimental, sewage-treatment plant. This effluent was very highly nitrified; the ammonia content was less than 1 ppm (N), and the nitrate content was 10.6 ppm (N). The average COD was 22.0 ppm.

The results of this series of experiments are presented in the following tables. Table VII shows the extent of COD elimination produced in the dark and upon subsequent irradiation.

Reaction in the dark - The results shown in Table VII indicate that substantial elimination of COD occurred during the initial period of chlorination in the dark. In some of the experiments, the indicated decrease in COD was equal to--or even greater than--the subsequent COD decrease which occurred upon irradiation. Although not all the experiments show large COD decreases during this period, (in fact, some show slight increases), there appears to be a statistically significant difference between the analytical figures obtained before and after chlorination in the dark; the average COD before chlorination was 20.8, the average after chlorination was 16.2. The difference between these figures represents a 22% average decrease in COD. A comparison of these averages is probably valid because it is not possible to correlate the individual COD decreases with differences in pH or differences in chlorine concentration.

TABLE VII

EXTENT OF COD ELIMINATION

Expt. No.	pH	Initial Chlorine Concentration (ppm)	Ultraviolet Irradiation Time (min.)	Extent of COD Elimination in Dark[a]		Extent of COD Elimination After Treatment in the Dark and After Irradiation[a]
				(ppm)	(%)	(%)
39	8.5	175	15	-5.23	27.1	49.5
40	8.5	102	10	-7.55	33.3	43.2
41	7.5	0	10	+0.61	[c]	0[b]
41	7.5	0	15	-2.70	[c]	13.0
42	8.5	102	15	+0.29	0[b]	35.7
43	6.5	175	10	-1.84	10.3	52.0
44	6.5	175	15	+0.70	0[b]	59.6
45	6.5	102	15	-1.98	9.4	68.8
46	6.5	102	10	-6.35	30.1	59.5
47	8.5	175	10	-5.55	29.9	53.8

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[a] The percentages were calculated after adjusting the initial COD values to account for the dilution which occurs when chlorine water is added.

[b] In these experiments, the slight increase in COD which was detected is within the range of experimental error.

[c] No "reaction in the dark" preceded irradiation.

However, we do not believe that the extent of oxidation in the dark was as great as these figures indicate. The main reason for doubt is that the amount of chlorine consumed during the same period is not sufficient to produce COD decreases of this magnitude. The elimination of 1 ppm of COD requires 4.43 ppm of chlorine. Inspection of the data presented in Table VIII clearly shows that the apparent COD elimination in this series of experiments was far greater than that which could be produced by the amount of chlorine consumed.

The apparent loss of COD in the dark was probably caused by a loss of volatile organic matter during the nitrogen purge. Except for the first sample (which obviously does not require dechlorination) and the final sample (which usually contained only traces of chlorine), each sample was acidified and purged with nitrogen in order to remove chlorine. We believe that this particular effluent was unique in that it contained relatively large quantities of volatile organic products.

TABLE VIII

COMPARISON OF COD ELIMINATION WITH CHLORINE CONSUMPTION IN THE DARK

Expt. No.	Chlorine Consumption (ppm)	Theoretical COD Elimination Equivalent to Chlorine Consumption (ppm)	Observed COD Elimination[a] (ppm)
39	7	1.58	5.23
40	10	2.26	7.55
42	3	0.68	0[b]
43	8	1.81	1.84
44	3	0.68	0[b]
45	7	1.58	1.98
46	7	1.58	6.35
47	5	1.13	5.55

---

[a] Initial COD values were adjusted to account for the dilution which occurs when chlorine water is added.

[b] In these experiments, the slight increase in COD which was detected is within the range of experimental error.

In general, the TOC analyses (Table IX) also show significant decreases during the 10-min. period in the dark. (Unfortunately, some of the TOC analyses in this series were obviously too high and had to be discarded.) However, the TOC samples were taken at the same time as the COD samples, and the two samples were subjected simultaneously to the dechlorination procedure. Therefore, the TOC data are subject to the same errors as the COD data.

In subsequent experiments, the TOC samples were taken separately and dechlorinated by acidification (to pH 1 with H_2SO_4), followed by treatment with excess sodium bisulfite. This procedure could not be used for the COD samples because excess bisulfite would interfere with the COD determination.

These subsequent experiments provided considerable information concerning the extent of oxidation which takes place during a 10-min. period of chlorination in the dark. From a total of 13 experiments with six different effluents, the following observations were made: (1) during the 10-min. period of chlorination in the dark, the extent of COD reduction averaged 12% and ranged from 0.8-20%; (2) the extent of TOC reduction during this time was, in general, less than the extent of COD reduction. The TOC reduction averaged 6% and ranged from 0-15.3%.

TABLE IX

EXTENT OF TOC ELIMINATION IN THE DARK AND UPON IRRADIATION [a]

Expt. No.	pH	Initial Chlorine Concentration (ppm)	Ultraviolet Irradiation Time (min.)	Extent of TOC Elimination in Dark (%)	Extent of TOC Elimination on Irradiation (%)
39	8.5	175	15	-8	[b]
40	8.5	102	10	-33	[b]
41	7.5	0	10	-	-10
41	7.5	0	15	-	-19
42	8.5	102	15	-4	-35
43	6.5	175	10	+3	-25
44	6.5	175	15	-8[c]	-50[c]
45	6.5	102	15	+9	+12
46	6.5	102	10	+14	-17
47	8.5	175	10	-22	-26

---

[a] Initial TOC values were adjusted to account for the dilution which occurs when chlorine water is added.

[b] The calculations for these experiments could not be made because the TOC results were obviously in error.

[c] These values were calculated assuming that the actual initial TOC in Experiment 44 was equal to average initial TOC value (9.11 ppm).

A summary of data concerning the extent of oxidation in the dark is presented in the Experimental section (see "Extent of Oxidation Produced by Chlorine in the Dark," p. 107).

Reaction during irradiation - When the UV lamp was placed in the immersion well, the chlorine concentration began to decrease rapidly (Table X). By far the greatest percentage of available chlorine was consumed during the first 5 min. Almost all the remaining chlorine was consumed during the second 5 min.; and, in almost every case, the small amount of residual chlorine was consumed during the final 5 min. of irradiation.

The extent of chlorine consumption during the first 5 min. (Table XI) was directly proportional to the chlorine concentration and was not related to the difference in pH. The extent of chlorine consumption during the second 5 min. was likewise directly related to the amount of chlorine present.

TABLE X

CHLORINE CONSUMPTION IN THE DARK AND DURING IRRADIATION

Expt. No.	Initial Chlorine Concentration (ppm)	Chlorine Consumption (ppm)[a] In the Dark (10 min.)	Upon Irradiation 0-5 min.	5-10 min.	10-15 min.
39	175	7	112	31	6
40	102	10	70	24	-
42	102	3	72	24	3
43	175	8	95	60	-
44	175	3	114	54	7
45	102	7	72	14	1
46	102	7	63	30	-
47	175	5	118	47	-

---

a/ In experiments in which the chlorine concentrations were not determined exactly at 5-min. intervals, the chlorine consumption during these periods was estimated.

TABLE XI

CHLORINE CONSUMPTION (PPM) DURING FIRST FIVE MINUTES OF IRRADIATION

(Experiments 39-47) a/

At pH 6.5		At pH 8.5	
175 ppm Cl_2	102 ppm Cl_2	175 ppm Cl_2	102 ppm Cl_2
95 (43)	63 (46)	118 (47)	70 (40)
114 (44)	72 (45)	112 (39)	72 (42)

---

a/ The individual experiment numbers are shown in parentheses.

Since practically all the chlorine was consumed during the first 10 min., the extent of organic oxidation during the 10-min. experiments would be expected to be similar to that which occurred during the 15-min. experiment. (As discussed below, the extent of organic oxidation produced by UV-radiation alone during the third 5-min. period would not be significant.) This postulation is confirmed by the results shown in Table XII.

Also indicated by the results presented in Table XII is the conclusion that no particular benefit is derived by the presence of a large excess of chlorine. This is perhaps the most important conclusion derived from this series of experiments.

Another conclusion drawn from the results shown in Table XII is that the oxidation is more effective at pH 6.5 than at pH 8.5; the average COD decrease at pH 6.5 was 60.0%, the average COD decrease at pH 8.5 was 45.6%. For these calculations, the results of both the 10-min. and the 15-min. experiments were combined. The results, 60.0% and 45.6%, are the approximate amount of COD elimination produced in 10 min. because, as indicated in Table X (p. 24), the chlorine had been almost completely consumed at the end of 10 min. As discussed below, an insignificant amount of COD elimination would be expected during the final 5 min.

TABLE XII

PERCENT ELIMINATION OF COD DURING IRRADIATION
(Experiments 39-47)

Total Irradiation Time, min.	At pH 6.5		At pH 8.5	
	175 ppm Cl_2	102 ppm Cl_2	175 ppm Cl_2	102 ppm Cl_2
10	52.0	59.5	53.8	43.2
15	59.6	68.8	49.5	35.7

Effect of irradiation alone - In Experiment 41, the effluent was irradiated as in the other experiments, but no chlorine was added. After 10 min., there was no detectable decrease in COD (the analytical results actually indicated 2.9% increase in COD which is considered to be within the range of experimental error). However, the TOC decrease was 10.4%. After 15 min., the COD decrease amounted to 13.0% and the TOC decrease was 18.8%. (Since the TOC decrease cannot theoretically exceed the COD decrease, one of these analytical results is obviously inaccurate.)

A comparison of the average COD decrease produced in 10 min. at pH 6.5 (60.0%) with the COD decrease produced by UV radiation alone during this time (2/3 x 13.0% = 8.66%) indicates that chlorine plus UV radiation is about seven times more effective than radiation alone. This result is consistent with the results of the first series of exploratory experiments, which indicated that chlorine plus UV radiation eliminated COD 10 times faster than radiation alone at pH 10, and more than eight times faster than UV radiation alone at pH 5.

THIRD SERIES OF WASTEWATER OXIDATION EXPERIMENTS

Summary

In the UV-catalyzed chlorine oxidation of wastewater, the organic oxidation rate is faster at pH 6.5 than at pH 3; and is faster at pH 5 than at pH 3 or pH 10.

Large excesses of chlorine do not increase the organic oxidation rate, except at pH 10. Most efficient use of chlorine was obtained when chlorine was added gradually during the irradiation period.

At pH 5 and pH 6.5, the rate of COD elimination is most rapid during the first 5 min. and decreases as the reaction proceeds. The elimination of TOC is approximately linear over a 15-min. irradiation period.

At pH 5, the average COD elimination was 67% in 5 min. (range 51-84%), 79% in 10 min. (range 66-100%), and 94.5% in 15 min. (range 88-100%). The average TOC decrease was 33% in 5 min. (range 15-50%), 52% in 10 min. (range 44-60%) and 75% in 15 min. (range 70-81%).

In the UV-catalyzed chlorine oxidation process, the rate and extent of organic oxidation is not affected by temperature within the range 5°-25°C (41°-77°F).

Third Series of Wastewater Oxidation Experiments

Some important questions were generated by the preceding series of experiments. Perhaps the most important question was "What extent of COD and TOC elimination occurs during the first 5-min. period of irradiation, the time during which the largest amount of chlorine is consumed?" Two other related questions were "Is the amount of organic material oxidized proportional to the amount of chlorine consumed?" and "Given a large excess of chlorine and an extended period of illumination, can all the organic material be eliminated?" Another important question was "Since pH 6.5 appears more effective than pH 8.5, would a further decrease in pH be even more effective?"

Experiments 48 and 49 - These experiments were designed to answer the above questions. Both experiments were performed using an effluent (S&L-6) which was obtained from the same source as the effluent used in Experiments 39 - 47. In Experiment 48 the pH level was maintained near 3.0, and samples were withdrawn at 5-min. intervals. Samples for TOC determination were not dechlorinated by nitrogen purge, but were treated with excess sodium bisulfite and acidified to pH 1 with H_2SO_4. Experiment 49 was similar, except that the pH was maintained at 6.5.

The results of these experiments are shown in Figures 9 and 10. The effect of pH on COD and TOC elimination was very marked. At pH 3.0, there was a 33% drop in COD and a 12% drop in TOC after 10-min. illumination. However, at pH 6.5, the COD elimination amounted to 72%, and the TOC elimination amounted to 54% during the same length of time.

Moreover, after only 5 min. at pH 6.5, the COD elimination amounted to 44% and the TOC elimination amounted to 38%. These results clearly show that the oxidation is much more effective at pH 6.5 than at pH 3.0.

The role of excess chlorine was further clarified by these experiments. After all the initial chlorine had been consumed, an additional amount of chlorine approximately equal to the initial chlorine dose was added to the reaction mixture. As is evident in Figures 9 and 10, no significant acceleration of either the COD or TOC elimination was caused by this addition of excess chlorine.

The results of these two experiments and the preceding series of experiments (Experiments 39 - 47) indicate clearly that the presence of excess chlorine is of no particular value.

Experiment 49 indicates that, at pH 6.5, the rate of oxidation of organic matter, as measured by both COD and TOC, decreases as the reaction progresses. In subsequent experiments at pH 5, the rate of COD elimination also decreased with time, but the rate of TOC elimination was approximately linear. Apparently, the organic constituents in a particular effluent vary widely in regard to the rate at which they are oxidized. Thus, the overall rate of oxidation decreases as the more-easily-oxidized material is consumed.

Also clarified by these experiments is the role of pH; decreasing the pH from 6.5 to 3.0 (Experiments 48 and 49), or raising the pH from 6.5 to 8.5, (Experiments 39 - 47) produces significant decreases in the oxidation rate. These conclusions were further substantiated in Experiments 52 - 54, described below.

Experiment 50 - The primary objective of Experiment 50 was to confirm the results of Experiment 49 using a municipal effluent which had been further processed in our laboratory-scale, extended-aeration apparatus.

The results (Figure 11) confirm that a very large proportion of the total COD and TOC elimination does occur during the first 5 min. of irradiation. Tables XIII and XIV present the results of experiments 49 and 50.

TABLE XIII

UV-CATALYZED CHLORINE OXIDATION OF AN EFFLUENT OBTAINED FROM A LARGE, SEWAGE-TREATMENT PLANT

(Effluent S&L-6, pH 6.5, Experiment 49)

Reaction Period	Chlorine Consumption (ppm)	COD Elimination (ppm)	COD Elimination (%)[a]	TOC Elimination (ppm)	TOC Elimination (%)[a]
During 10 min. in dark	10	0.2	0.8	0.04	0.5
During first 5-min. irradiation	80	11.1	44.0	2.8	37.7
During second 5-min. irradiation	35	7.0	27.7	1.2	16.1
Totals after 20 min.	125	18.3	72.5	4.04	54.3

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[a] The percent figures were calculated by dividing the amount of COD (or TOC) eliminated during each 5-min. interval by the original COD (or TOC) value (corrected for the dilution effect caused by added chlorine).

TABLE XIV

UV-CATALYZED CHLORINE OXIDATION OF AN EFFLUENT FROM A LABORATORY-SCALE, SEWAGE-TREATMENT APPARATUS

(Effluent MRI-428, pH 6.5, Experiment 50)

Reaction Period	Chlorine Consumption (ppm)	COD Elimination (ppm)	COD Elimination (%)[a]	TOC Elimination (ppm)	TOC Elimination (%)[a]
During 10 min. in dark	6	0.76	2.9	0.6	5.7
During first 5-min. irradiation	137	19.43	73.5	4.6	43.5
During second 5-min. irradiation	21	2.72	10.2	2.0	18.9
Totals after 20 min.	164	22.91	86.6	7.2	68.1

---

[a] The percent figures were calculated by dividing the amount of COD (or TOC) elimination during each 5-min. interval by the original COD (or TOC) value (corrected for the dilution effect caused by added chlorine).

Three important observations were made, based on the results of Experiments 49 and 50.

(1) There was very little consumption of chlorine or elimination of COD or TOC during the 10-min. period of chlorination in the dark. Thus, these two effluents contained relatively small amounts of organic material which could be oxidized in the dark. As discussed in the previous section, the average amount of TOC and COD elimination produced during the 10-min. period of chlorination in the dark was 10%. (See Experimental Section, "Extent of Organic Oxidation Produced by Chlorine in the Dark", p. 108.)

(2) Large amounts of TOC and COD elimination were produced during the initial 5-min. period of irradiation. For the Smith and Loveless effluent, 44% COD elimination and 38% TOC elimination occurred during this time. For the effluent produced in the laboratory-scale, activated-sludge apparatus, 74% COD elimination and 44% TOC elimination was produced during this initial 5-min. period of irradiation.

(3) Less COD and TOC elimination is produced during the second 5-min. period of irradiation. Elimination of COD during the second 5-min. period was 27.7% for the Smith and Loveless effluent, and 10.2% for the laboratory-produced effluent. Elimination of TOC during this time was 16.1% for the Smith and Loveless effluent, and 18.9% for the laboratory-produced effluent.

Further investigation of the effect of pH - Three experiments (Experiments 52 - 54) were designed to investigate the rate and extent of UV-catalyzed chlorine oxidation at pH 3, pH 5 and pH 10. The effluent (MRI-512) used in these experiments contained 33.8 mg/liter COD, 13.2 mg/liter TOC, 2.5 mg/liter ammonia nitrogen and 4.0 mg/liter nitrate nitrogen (average values). It had been produced in our laboratory by passing high-ammonia municipal wastewater through the laboratory-scale, activated-sludge apparatus. In each experiment the effluent was treated with chlorine water to provide an initial chlorine concentration of about 200 ppm. This concentration represents a 33% excess over the theoretical amount of chlorine required to oxidize all of the organic material to CO_2 and H_2O. The results of a second addition of chlorine will be discussed in the next section, "Effect of Chlorine Concentration", p. 32.

The experiments were performed at room temperature and were identical, except that each was performed at a different pH (pH 3, pH 5, and pH 10). During the 10-min. period of chlorination in the dark, the average chlorine concentration decreased about 26 ppm. During this time, there was an average decrease in COD of 3.6 mg/liter (12%) and an average decrease in TOC of 0.3 mg/liter (3%). These results in the dark were about the same in each experiment, except that the chlorine consumption and the extent of TOC decrease were somewhat greater at pH 10.

The results of these experiments are shown in Figures 12 - 14, and the data are summarized in Figures 15 and 16. The results presented in Figure 15 indicate that the rate of COD elimination upon irradiation is the fastest at pH 5; approximately 70% of the COD present after treatment with chlorine in the dark was eliminated during 5 min. of irradiation, and 80% was eliminated within 10 min.

The extent of TOC elimination in these experiments is shown in Figure 16. These results are in agreement with the COD data; more rapid TOC elimination is produced at pH 5 than at pH 3 or at pH 10. However, the extent of TOC elimination is not as great as the extent of COD elimination. A curious fact is that the TOC plots are almost linear, while the rate of COD elimination decreases as the oxidation proceeds.

In these three experiments, the rate of chlorine consumption was about the same at all pH values; about two-thirds of the initial chlorine was consumed after 5 min. of irradiation, and practically all the initial chlorine was consumed after 10 min. of irradiation. Obviously, because of the large extent of organic oxidation, the most efficient utilization of chlorine was obtained at pH 5.

Subsequent experiments have confirmed that pH 5 is the optimum pH for the most efficient chlorine utilization and organic oxidation. These experiments are described in detail later in this report, and a summary of the data concerning the extent of organic oxidation is presented in the Experimental section (see "Extent of COD and TOC Elimination Produced by Irradiation at pH 5", p. 109). Seven experiments, using four different effluents, are compared. The data are presented graphically in Figures 17 and 18.

These figures show that the average COD elimination at pH 5 is 67% in 5 min., 79% in 10 min. and 95% in 15 min. The concurrent TOC elimination is 33% in 5 min., 52% in 10 min. and 75% in 15 min.

The data presented in these figures (Figures 17 and 18) confirm the observations of Experiments 52 - 54 that the rate of COD elimination decreases as the oxidation proceeds, but that the rate of TOC elimination is linear.

Effect of chlorine concentration - In general, the elimination of COD and TOC and the consumption of chlorine are most rapid at the beginning of the UV-catalyzed oxidation. However, the rate of organic oxidation is not directly proportional to the chlorine concentration; in the second series of eight experiments described in the preceding section, a 75% excess of chlorine produced no more organic oxidation in 10 min. than did a stoichiometric amount of chlorine.

The results of other experiments in this series have indicated that large increases in the initial chlorine concentration do not produce correspondingly large increases in organic oxidation rates. In Experiments 48 and 49, a second addition of chlorine approximately equal to the original amount of chlorine was added to the reaction mixtures after the reaction mixtures had been irradiated for about 10 min. No significant increase in organic oxidation rate was observed.

In Experiments 52 - 54, a second addition of chlorine was made, and the results at pH 5 (Experiment 54) and at pH 3 (Experiment 52) were similar to the results of Experiments 48 (pH 3.0) and 49 (pH 6.5). However, at pH 10 (Experiment 53), the second addition of chlorine actually did increase the rate of COD elimination. The rate of TOC elimination, however, was not affected.

Analysis of the above results indicates that, at pH values between 3.0 and 8.5, (1) only a certain minimum concentration of chlorine is required for maximum oxidation rate, and (2) concentrations of chlorine above this minimum are wasteful.

These conclusions are substantiated by an experiment (Experiment 78) in which the chlorine water was not added in one portion, but was added gradually in increments during the irradiation period. The results, presented in Figure 19, show conclusively that extensive elimination of COD (88% in 15 min.) and TOC (70% in 15 min.) can be achieved even when the concentration of chlorine does not exceed 36 ppm. The amount of chlorine consumed in this reaction was equivalent to approximately 89% of the total amount added. This amount of chlorine is only slightly in excess of the theoretical amount of chlorine (145 ppm) required to eliminate all of the original COD (32.9 ppm).

Thus, for the most efficient use of chlorine, a gradual addition of chlorine during irradiation is necessary.

The chlorine consumed, but yet not accounted for by an equivalent amount of organic oxidation, is most probably consumed by auto-decomposition reactions. The fact that chlorine is decomposed by ultraviolet radiation is well known, and the products are known to be chloric acid, hydrochloric acid and oxygen.6/ The extent to which chlorine alone is decomposed in our reactor is shown in Figure 20. Note that the decomposition is very much faster at pH 10 than at pH 5.

Effect of nitrate concentration - Because effluents contain varying concentrations of nitrate, it was important to learn whether or not variations in nitrate concentration could be responsible for observed variations in the rates of COD and TOC elimination. In one experiment (Experiment 77, Figure 21), 20 ppm of nitrate nitrogen (as potassium nitrate) was added to an effluent prior to treatment with chlorine. The effluent (S&L 624A) was the same as the one used in Experiment 75 (Figure 22). A comparison of Figures 21 and 22 shows that the rate of COD elimination and the rate of chlorine consumption are practically the same in each experiment. Therefore, within the range of 4-20 ppm, nitrate concentration has no effect on the rate or extent of the UV-catalyzed chlorine oxidation.

Effect of temperature - Two effluent oxidation experiments (Experiments 58 and 59) were performed in exactly the same manner, except that in one the temperature was held near 5°C (41°F) and in the other the temperature was held near 25°C (77°F). The results are shown in Figures 23 and 24. These figures show that the rate of chlorine consumption, rate of COD elimination, and rate of TOC elimination are practically the same at both temperatures. The temperatures of most effluents from extended aeration processes would be within the temperature range investigated. Therefore, in actual operation, ordinary temperature changes should have no effect on the rate of effluent oxidation.

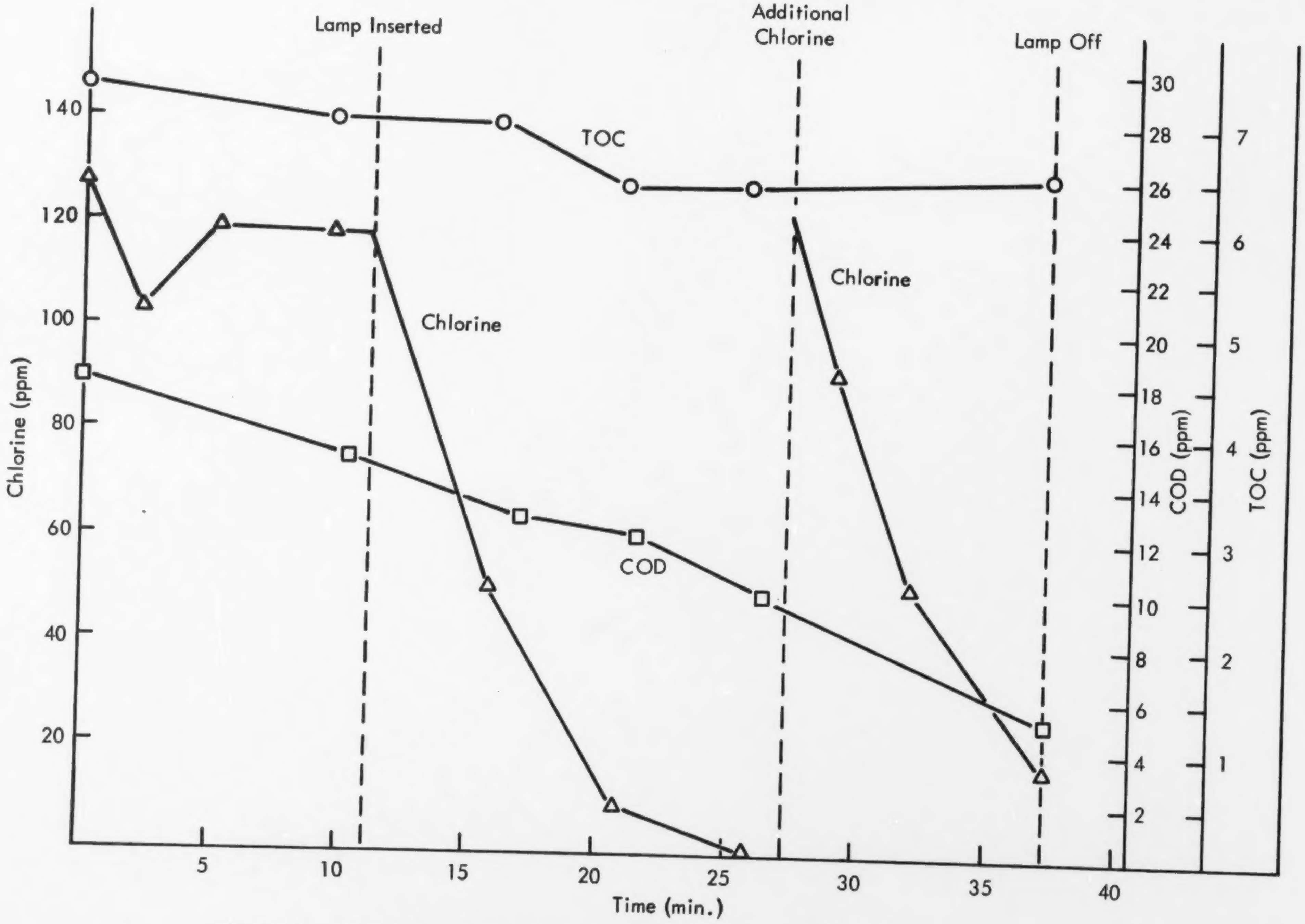

Figure 9 - UV-Catalyzed Chlorine Oxidation of Effluent S&L-6-A at pH 3.0 (Experiment 48)

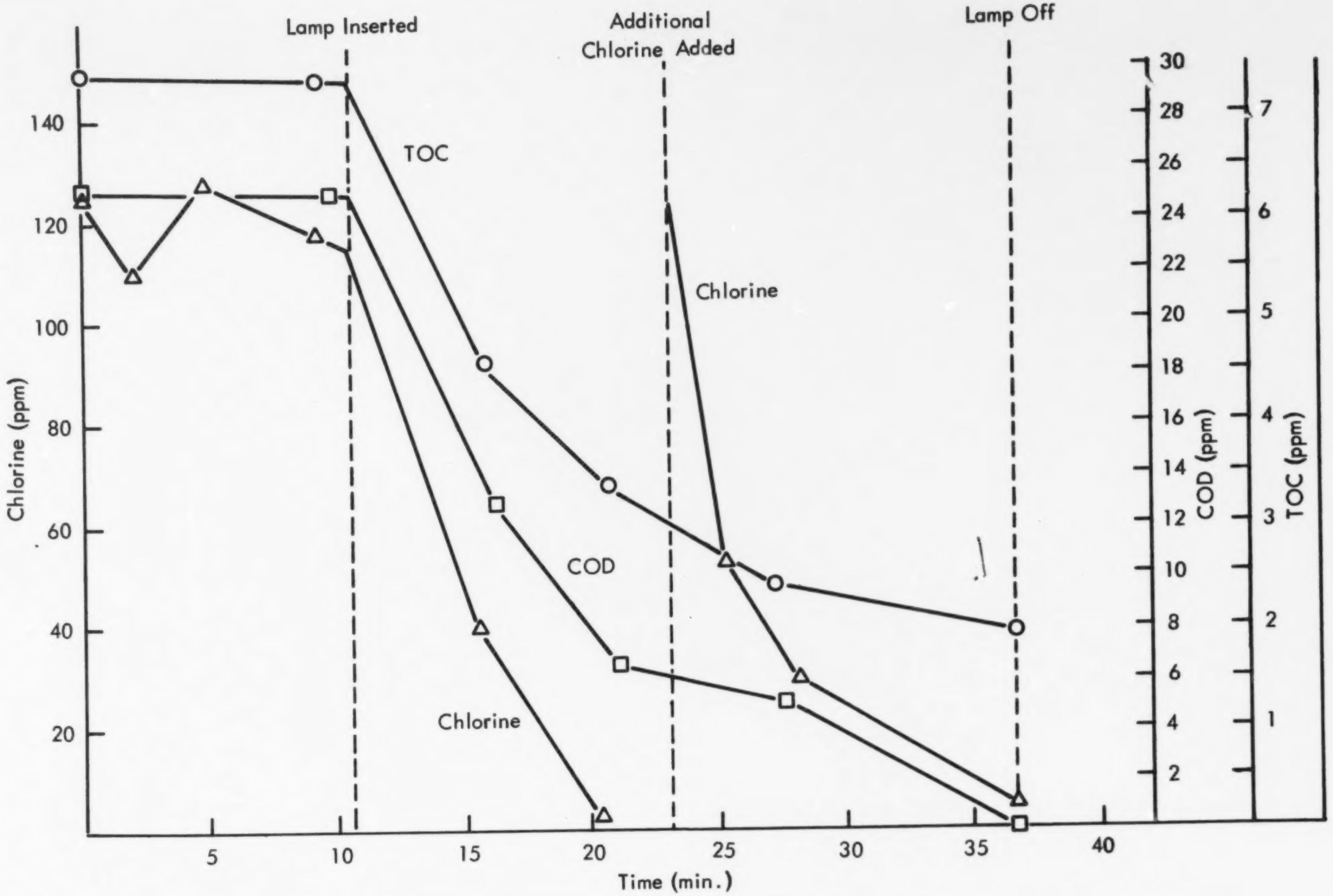

Figure 10 - UV-Catalyzed Chlorine Oxidation of Effluent S&L-6-A at pH 6.5 (Experiment 49)

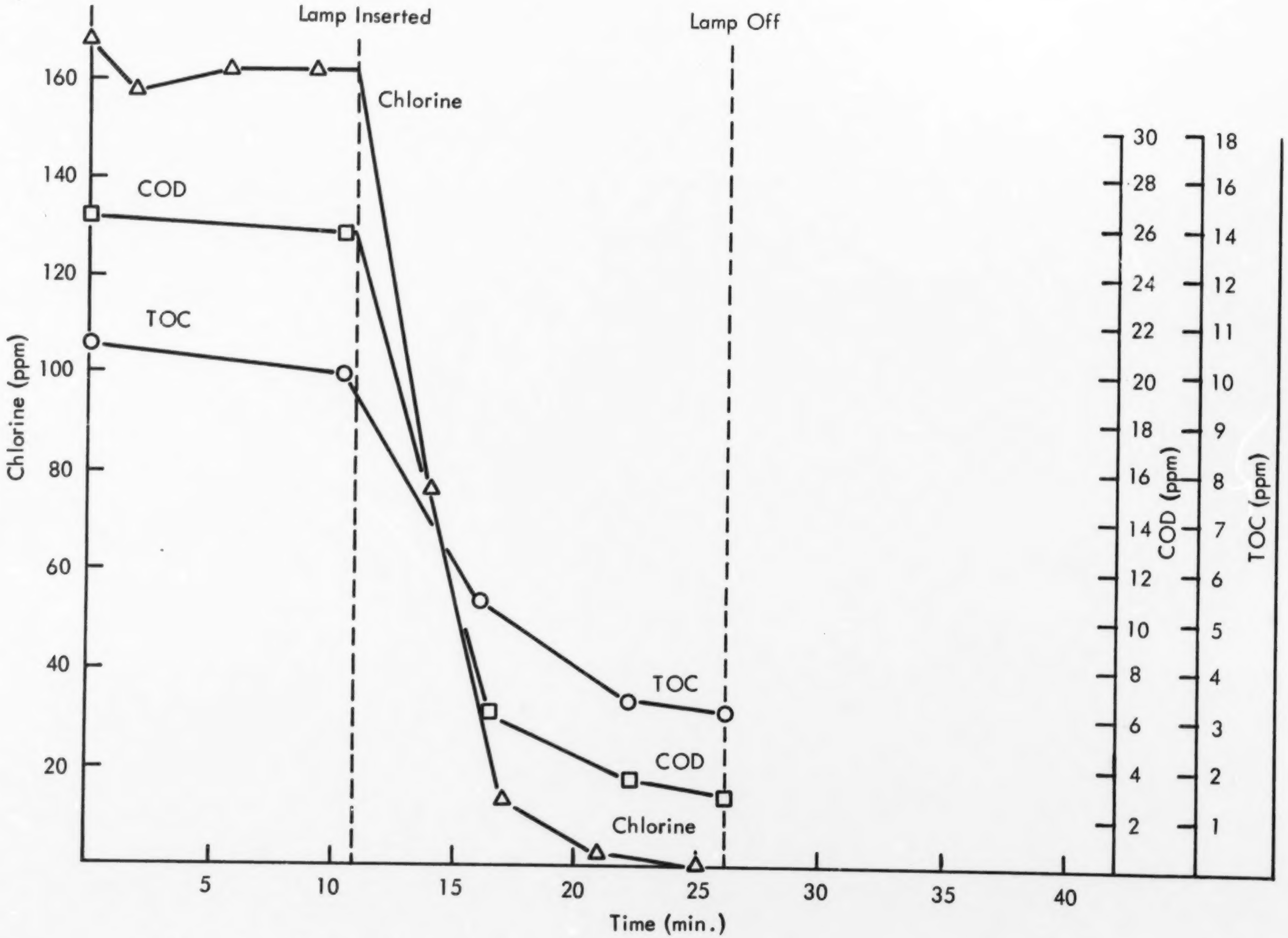

Figure 11 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-428 at pH 6.5 (Experiment 50)

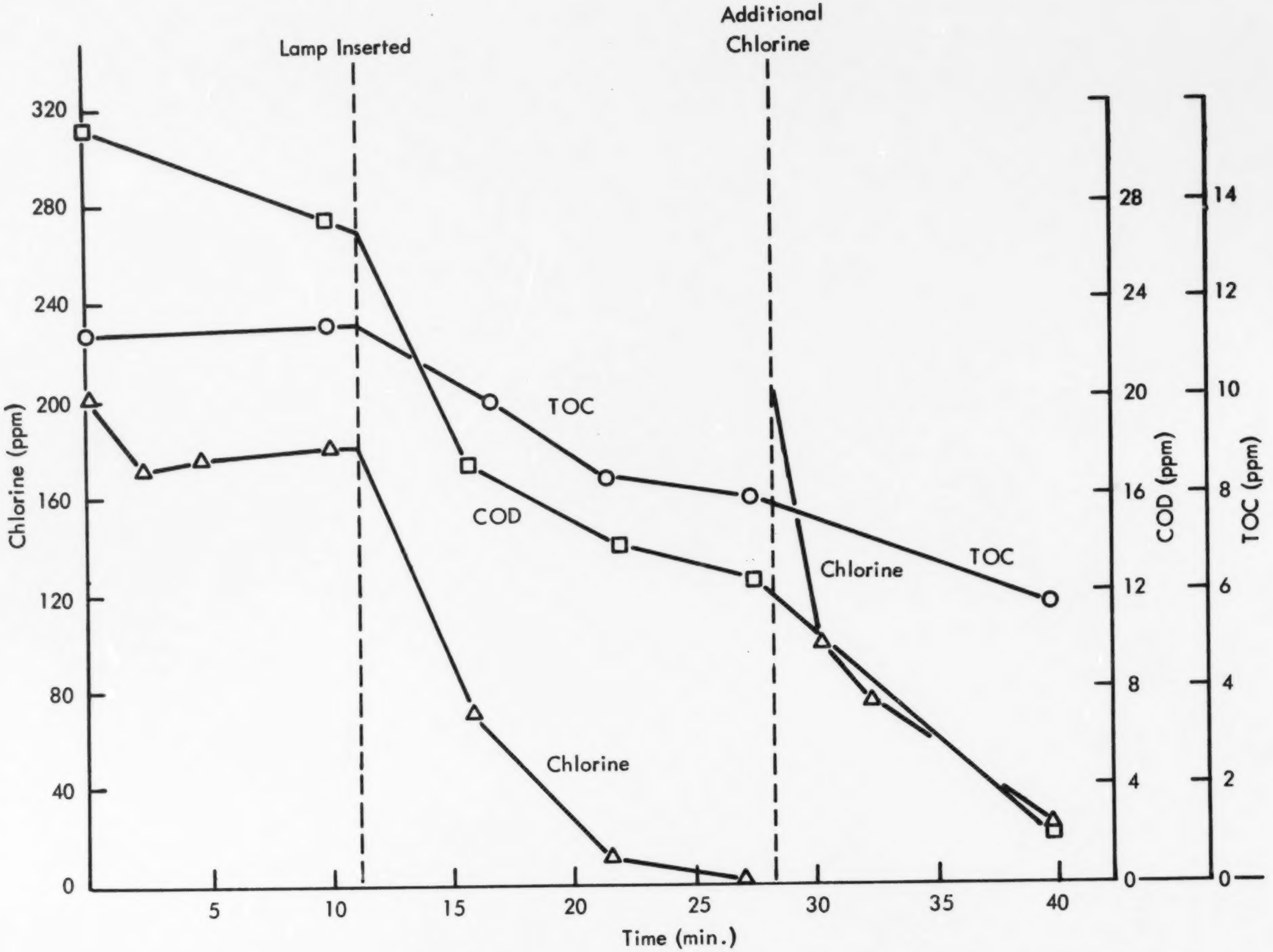

Figure 12 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-512 at pH 3 (Experiment 52)

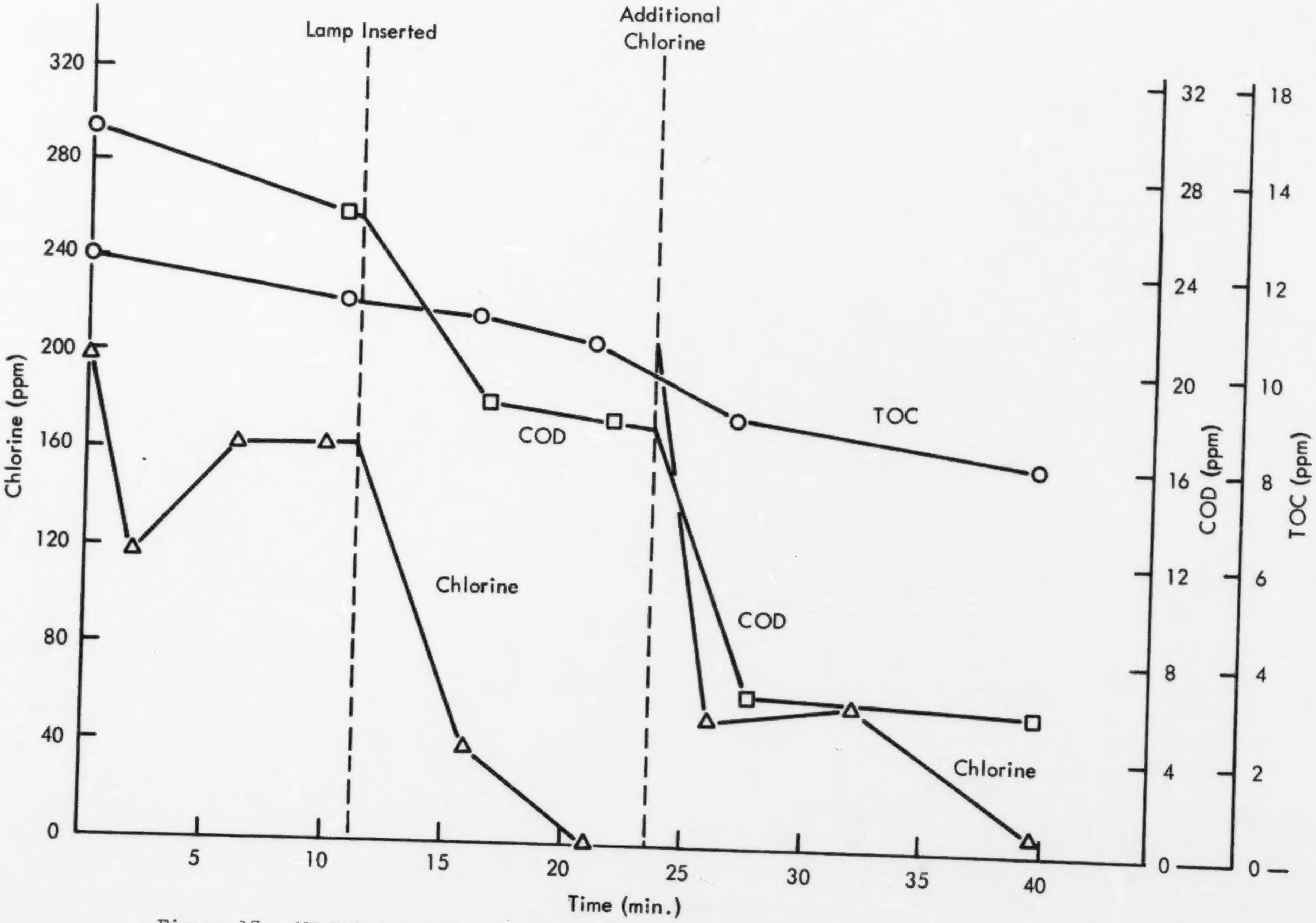

Figure 13 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-512 at pH 10 (Experiment 53)

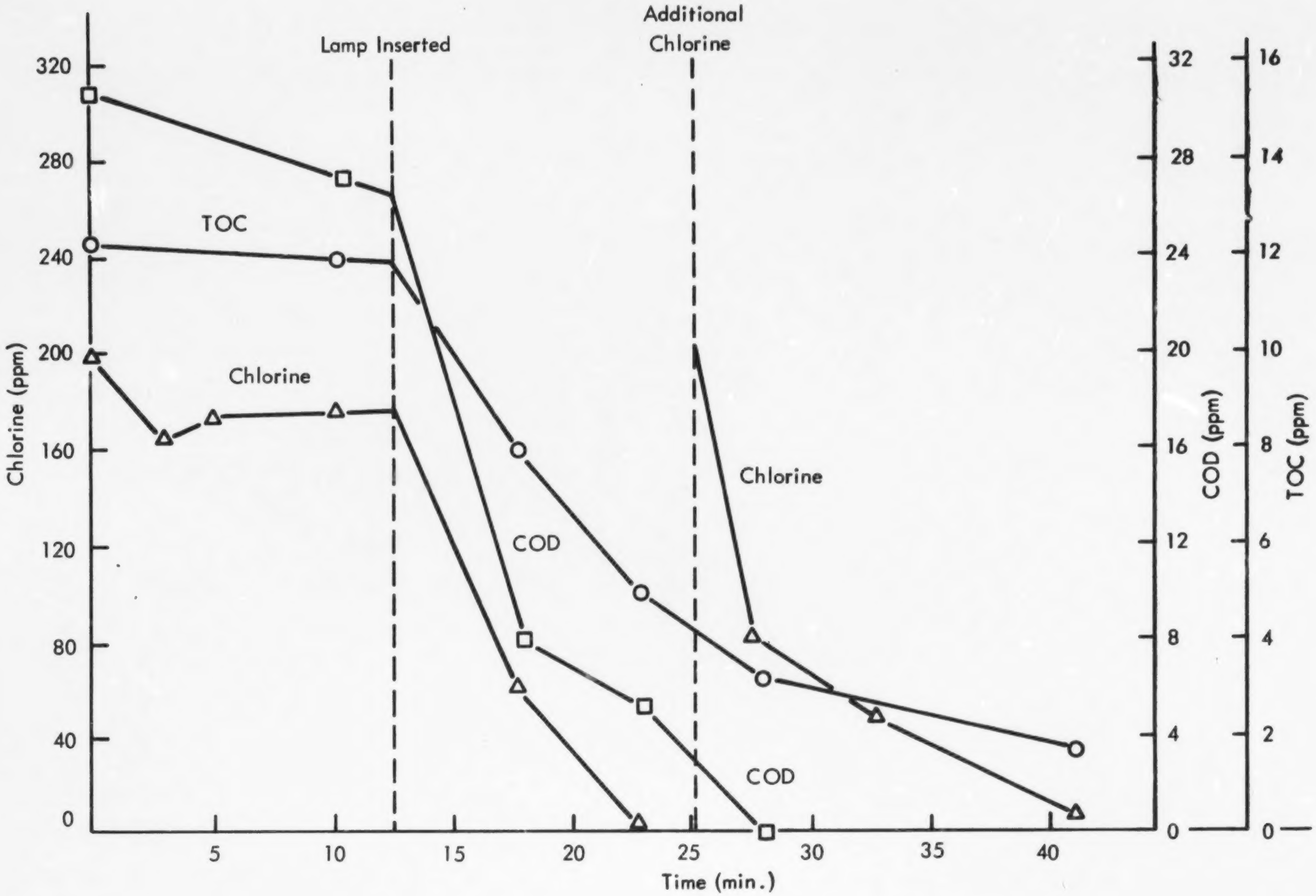

Figure 14 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-512 at pH 5 (Experiment 54)

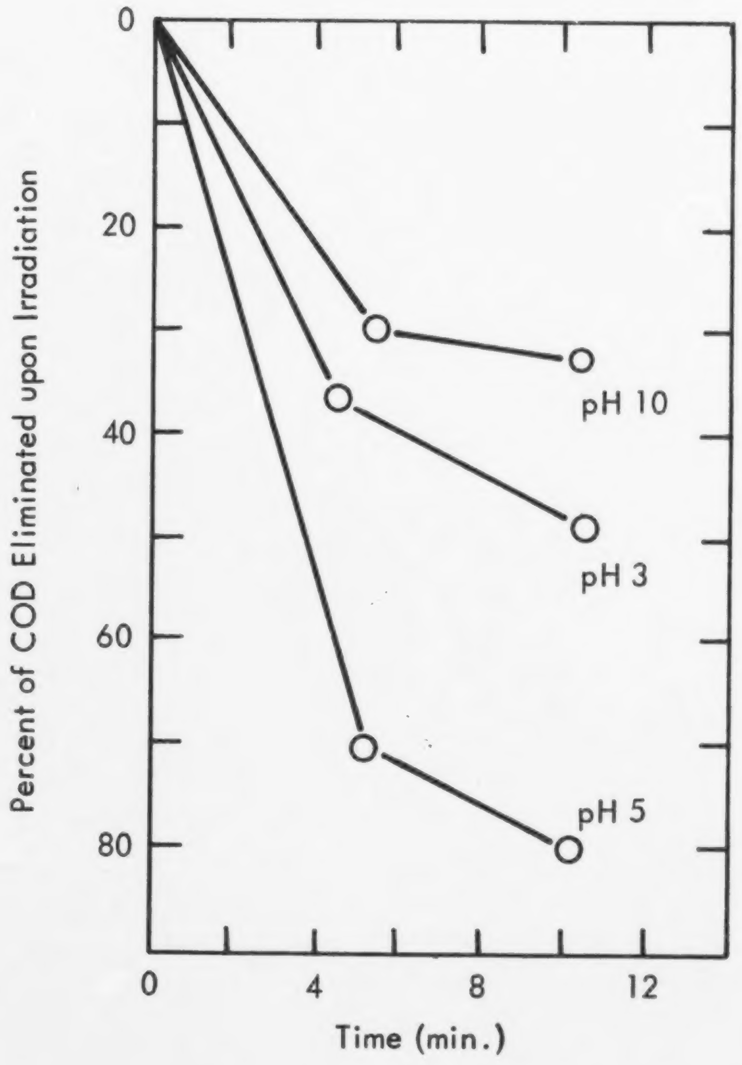

Figure 15 - Extent of Chemical Oxygen Demand (COD) Elimination Produced by UV-Catalyzed Chlorine Oxidation

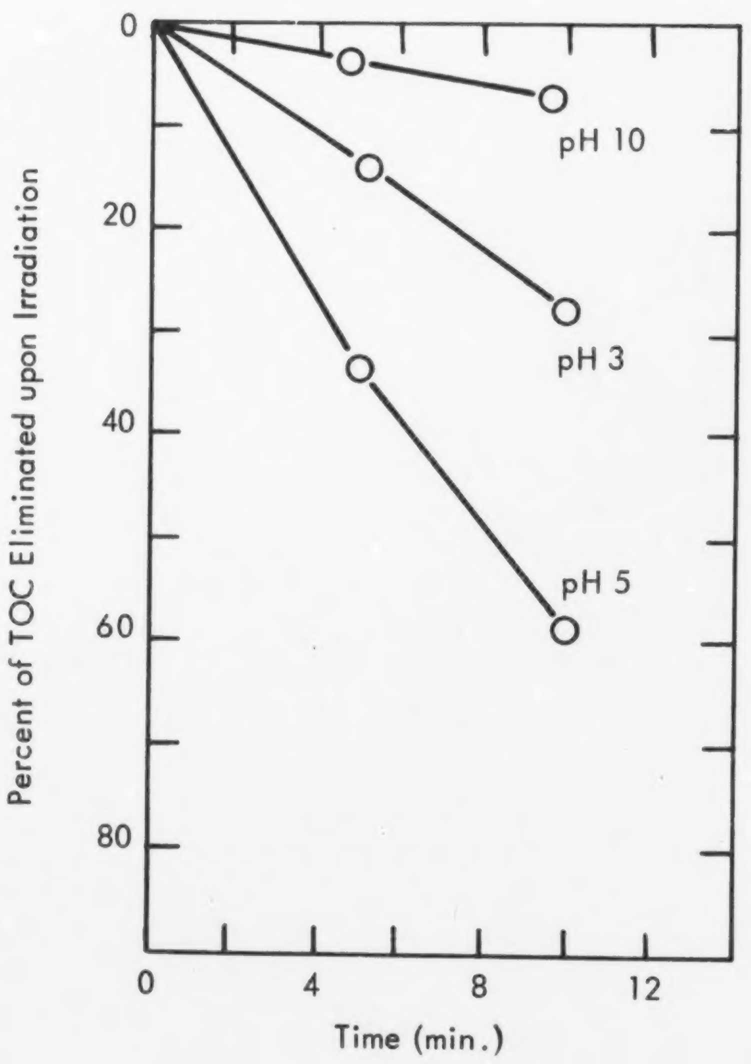

Figure 16 - Extent of Total Organic Carbon (TOC) Elimination Produced by UV-Catalyzed Chlorine Oxidation

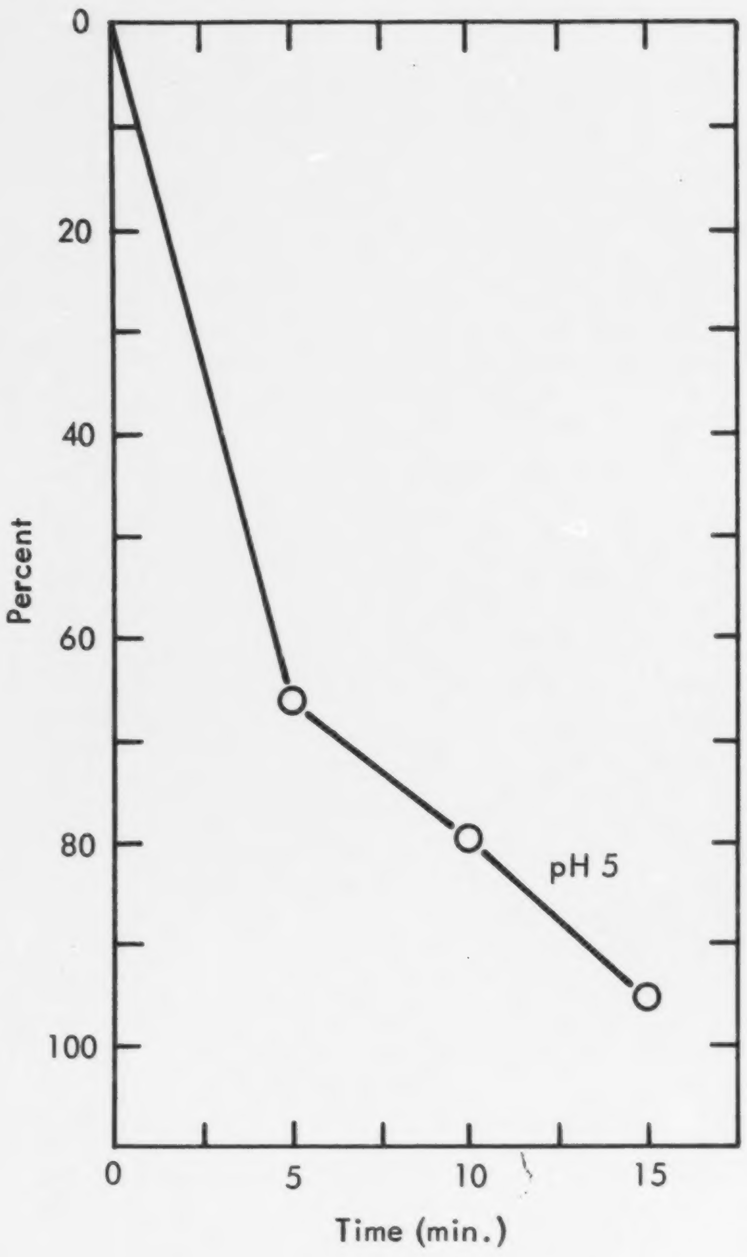

Figure 17 - Average Percent of COD Eliminated Upon Irradiation at pH 5

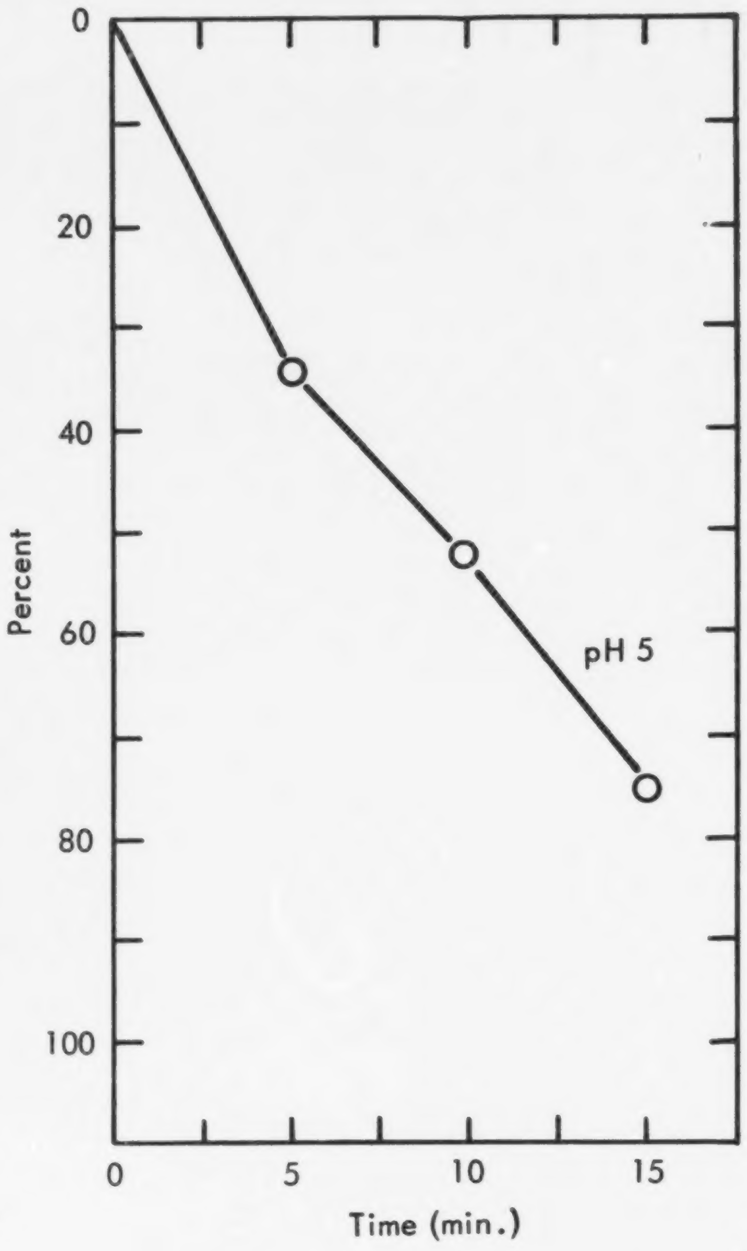

Figure 18 - Average Percent of TOC Eliminated Upon Irradiation at pH 5

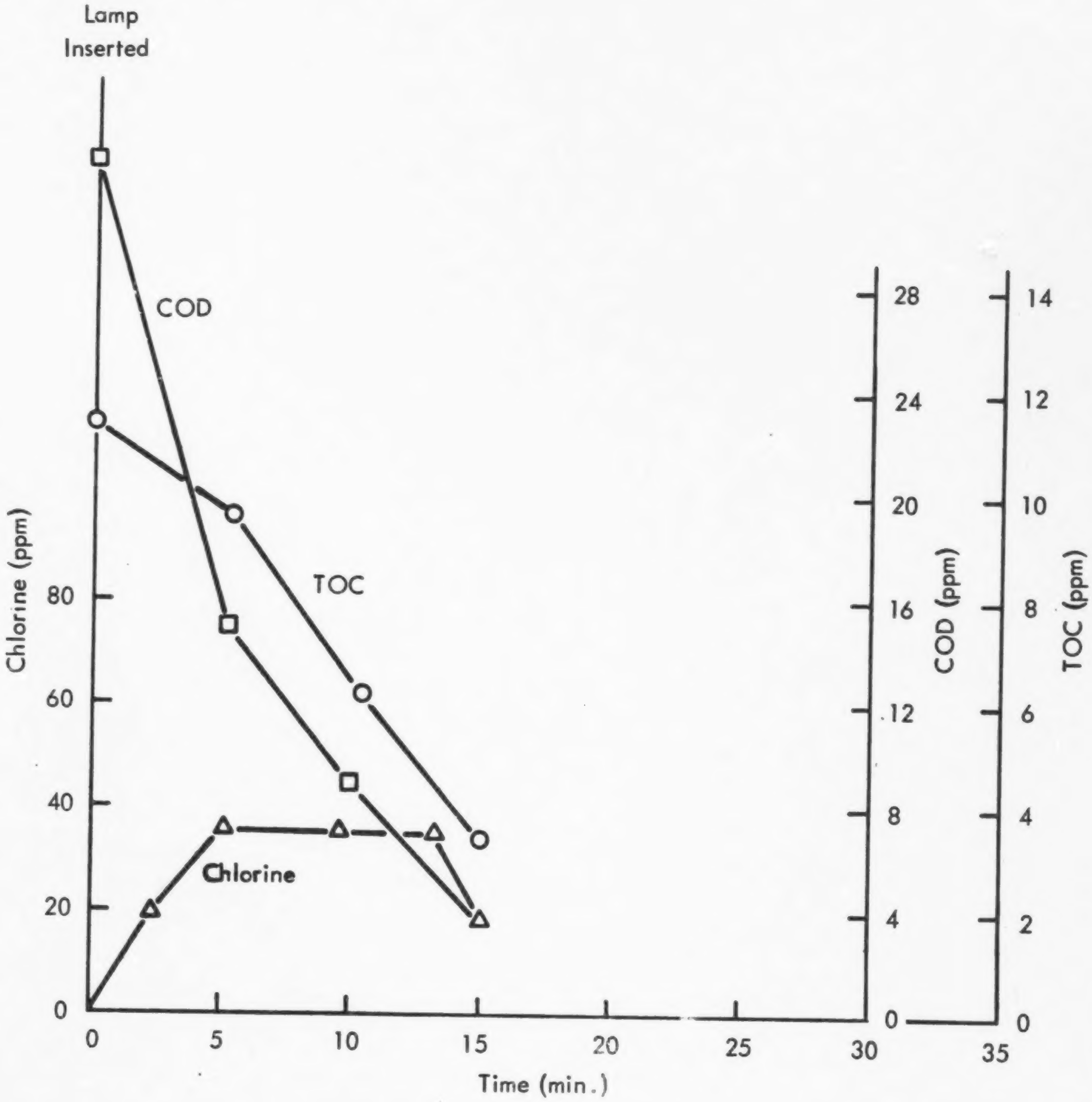

Figure 19 - UV-Catalyzed Chlorine Oxidation of Effluent S&L-624-A at pH 5 With Continuous Addition of Chlorine (Experiment 78)

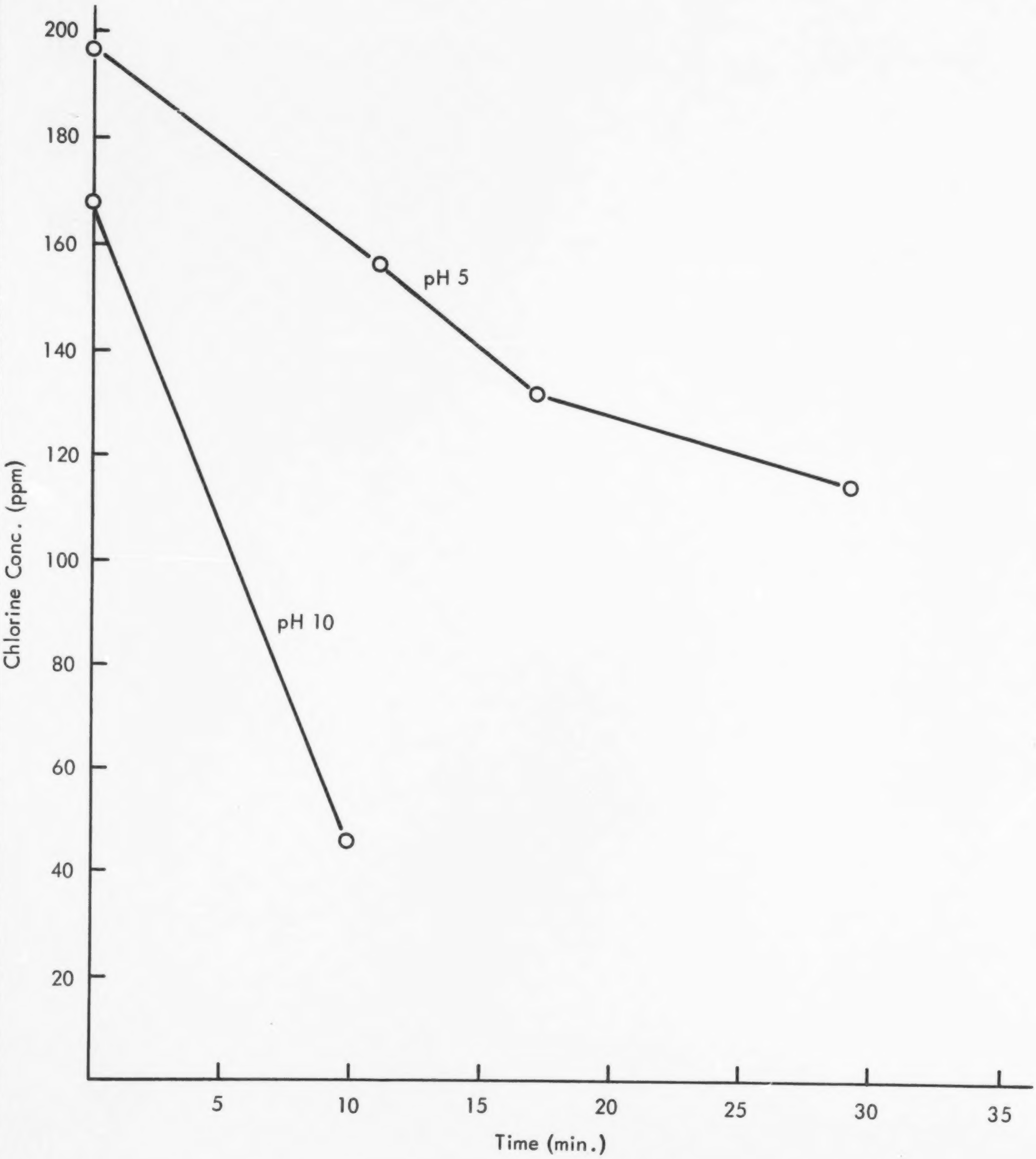

Figure 20 - Rates of Chlorine Decomposition During Irradiation at pH 5 and at pH 10

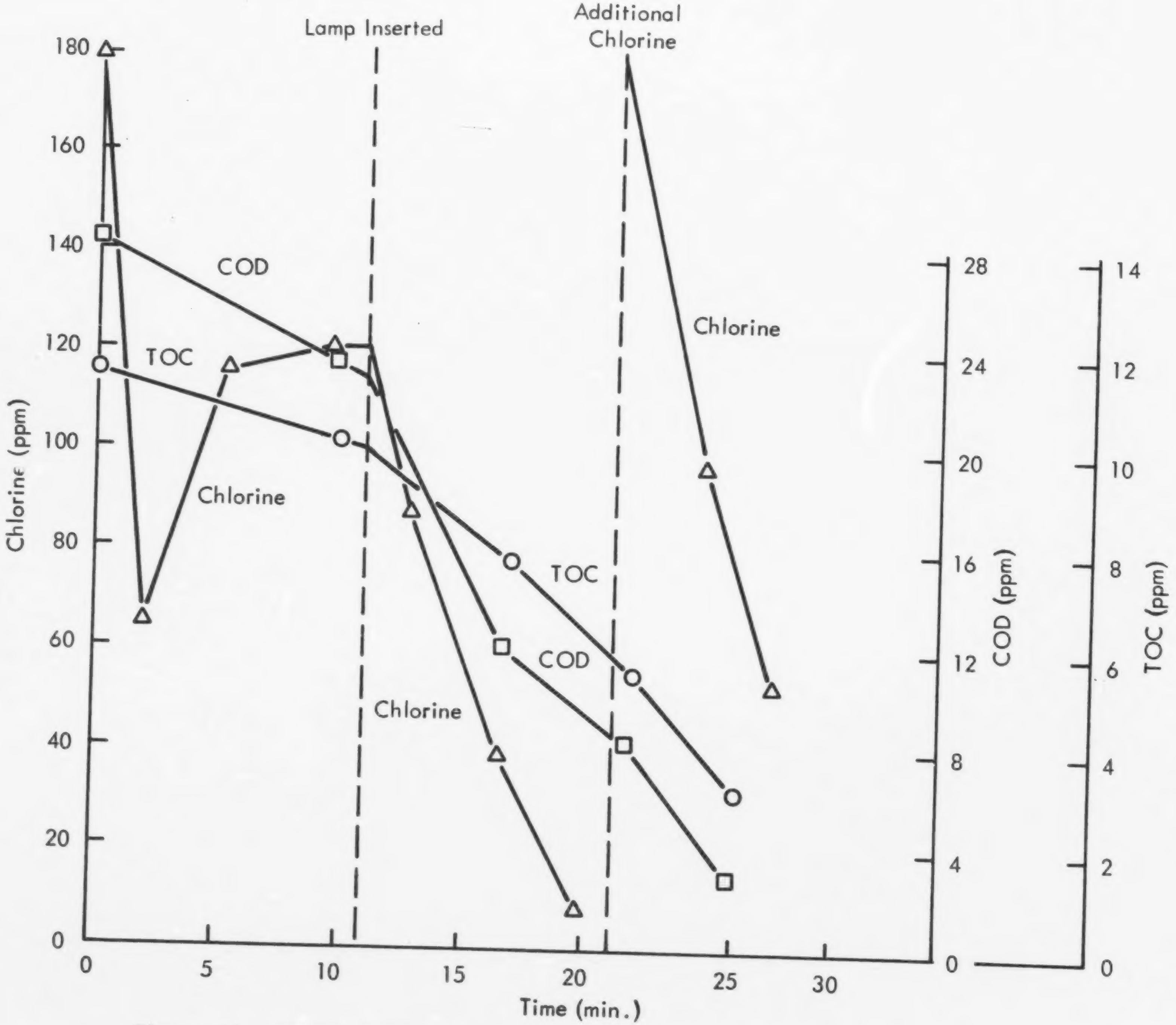

Figure 21 - UV-Catalyzed Chlorine Oxidation of Effluent S&L-624-A, Containing 20 ppm of Added Nitrate Nitrogen, at pH 5 (Experiment 77)

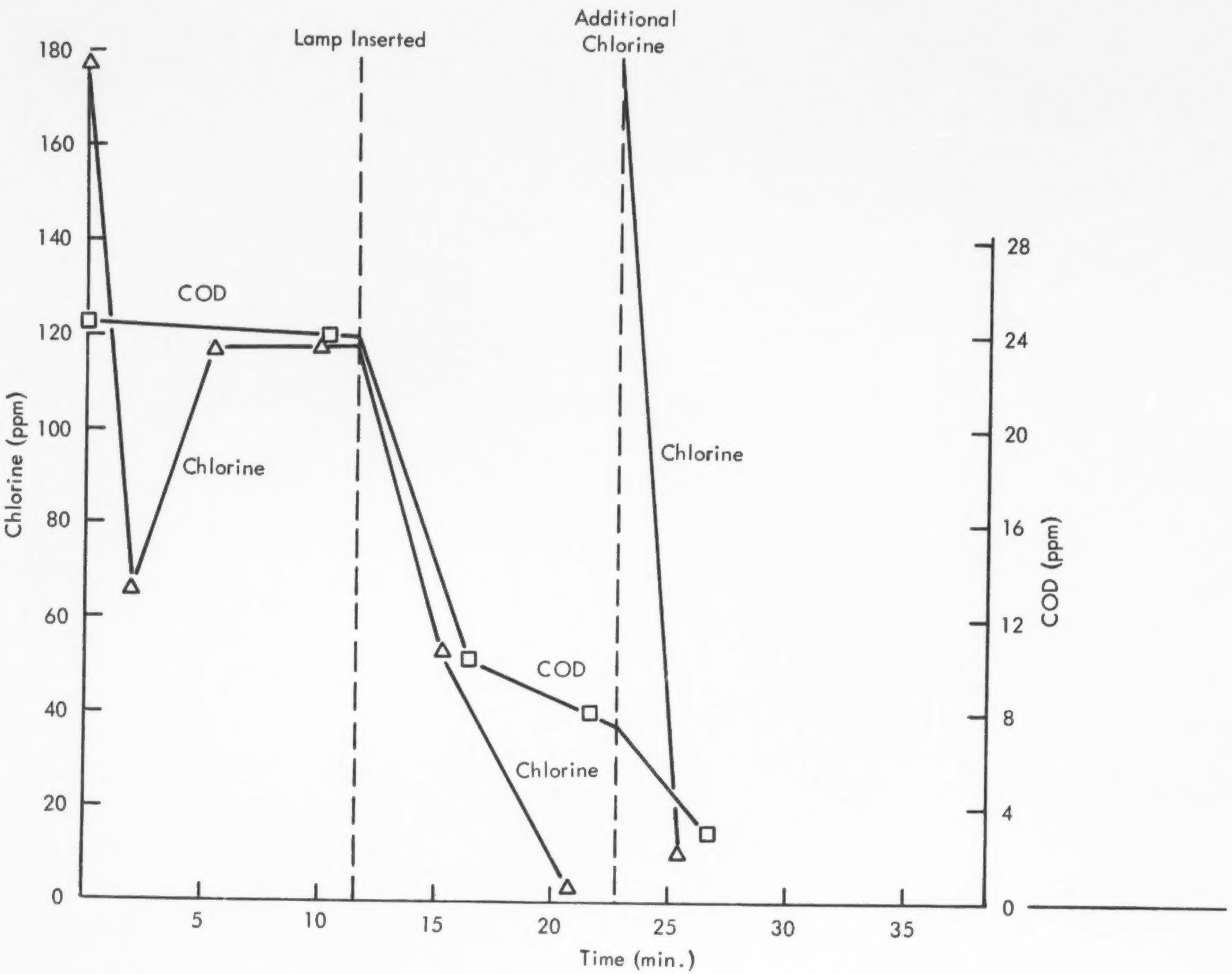

Figure 22 - UV-Catalyzed Chlorine Oxidation of Effluent S&L-624-A at pH 5 (Experiment 75)

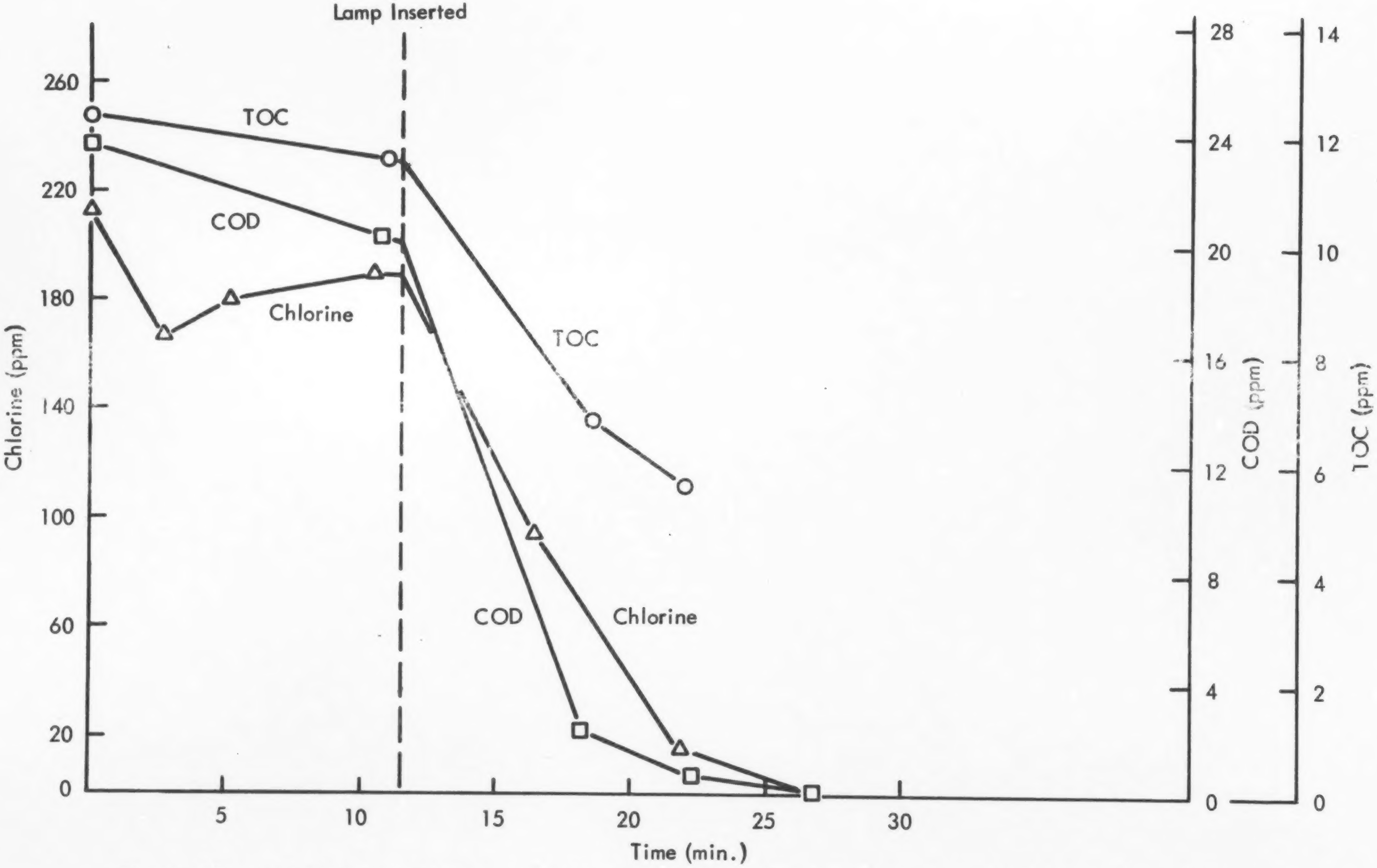

Figure 23 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-525 at pH 5 and 5°C (Experiment 58)

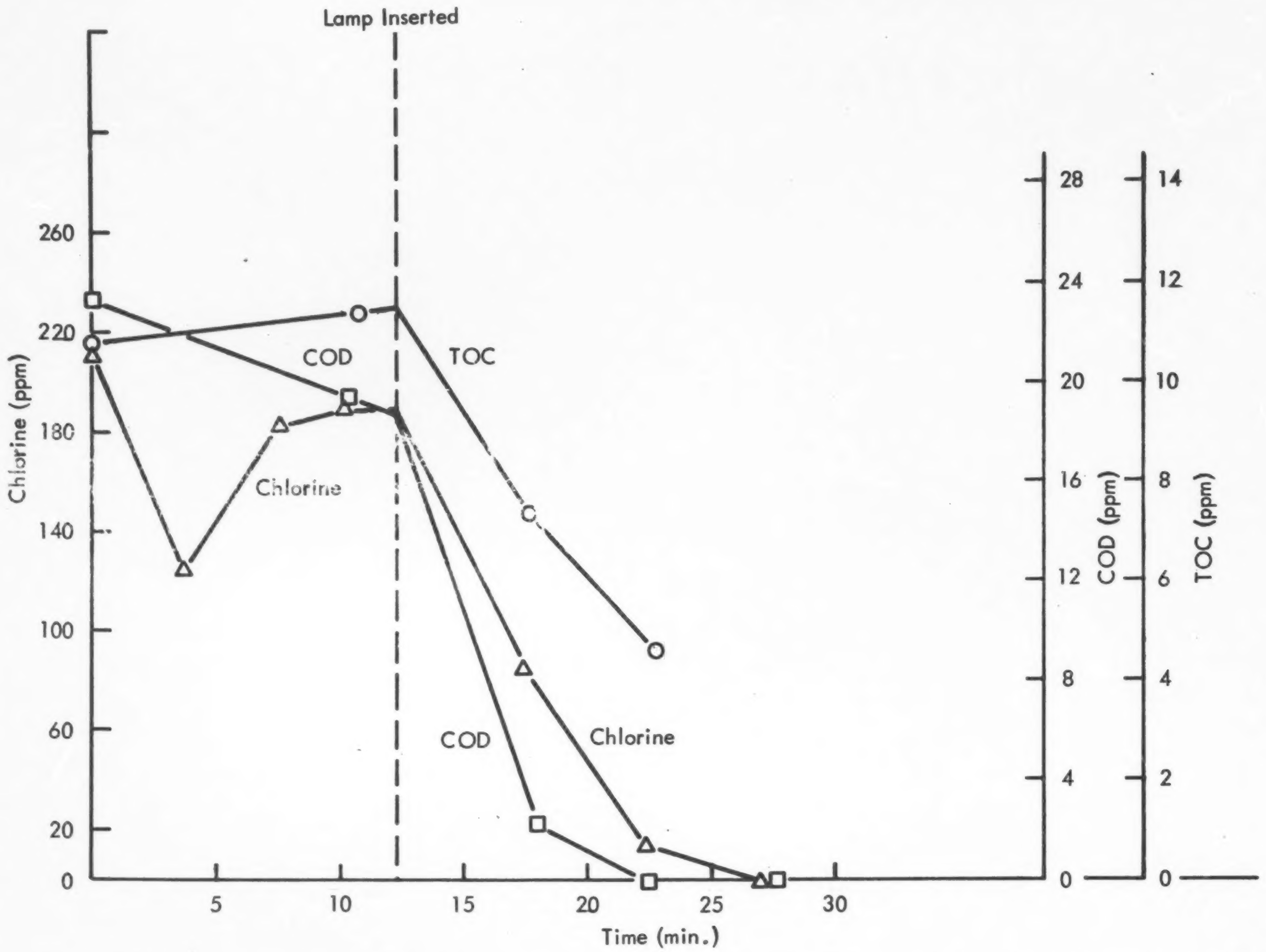

Figure 24 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-525 at pH 5 and 20°-25° (Experiment 59)

ULTRAVIOLET-CATALYZED CHLORINE OXIDATION OF HIGH-AMMONIA EFFLUENTS

Summary

The presence of ammonia in an effluent drastically reduces the rate and extent of UV-catalyzed chlorine oxidation of organic matter. For example, the addition of 23 ppm of ammonia nitrogen to a highly nitrified effluent reduced the organic oxidation rate by more than tenfold. The amount of chlorine actually required to eliminate 1 ppm of ammonia in the UV-catalyzed process is about four times the theoretical amount required to eliminate 1 ppm of COD.

Ultraviolet-Catalyzed Chlorine Oxidation of High-Ammonia Effluents

Municipal, sewage-treatment plants are frequently overloaded and often produce effluents which contain relatively high concentrations of ammonia (15-30 ppm N). Although it was known in advance that the treatment of effluents of this kind would not be economical, several oxidation experiments were performed with high-ammonia effluents for the purpose of determining: (1) the effect of relatively high, ammonia concentrations (15-30 ppm N) on the elimination of COD and TOC; and (2) the technical feasibility of using chlorine to produce a low-ammonia effluent for use in the laboratory.

When wastewater containing about 15 ppm ammonia nitrogen and having a COD of about 50 ppm is treated with about 180 ppm of chlorine in the dark, the concentration of "free" chlorine decreases rapidly, ammonia is simultaneously converted to chloramines, and a gradual increase in nitrate concentration begins. Irradiation produces a further rapid decrease in the chlorine concentration and a rapid increase in the nitrate concentration. These results were observed both at pH 5 (Experiment 20) and at pH 10 (Experiment 21). In these experiments, only about a 50% decrease in COD was produced after about 15 min. irradiation.

The elimination of 1 ppm of COD requires 4.43 ppm of chlorine, assuming complete conversion of the organic matter to carbon dioxide. If it is assumed that ammonia is oxidized to nitrogen gas, 1 ppm of ammonia nitrogen requires 7.6 ppm of chlorine. The oxidation of 1 ppm ammonia nitrogen to nitrate requires 20.3 ppm of chlorine.

Thus, the calculated chlorine "demand" for the effluent used in these experiments was 114 ppm of chlorine for the ammonia and 222 ppm for the COD. However, only about one-half (180 ppm) of the theoretical amount of chlorine was applied. Since about 60% of the chlorine consumed was theoretically required for the COD elimination, presumably the remainder was consumed in the oxidation of ammonia and by autodecomposition.

Similar results were obtained with other effluents. In Experiment 23, after 15 min. in the dark followed by 15 min. of irradiation, the decreases in ammonia (down 76%) and COD (down 30%) accounted for 95% of the chlorine consumed.

The undesirable effect of ammonia on the elimination of COD is apparent in all three of these experiments: in order to eliminate 1 ppm of COD, approximately 7.5 ppm of chlorine was required; this was about 170% more than the theoretical amount.

Even poorer efficiency of COD elimination was achieved in Experiments 27 and 30; elimination of 1 ppm of COD required about 11 ppm of chlorine, or 2.5 times the theoretical amount. In these two experiments, only about 40% of the chlorine was used for COD elimination; the remainder was consumed in ammonia oxidation.

Subsequent experiments were designed for the purpose of removing ammonia from the effluents by means of treatment with chlorine. The objective was not to find an economical process for removing ammonia, but to produce--in the laboratory--a low-ammonia effluent for further investigation.

Experiment 27 showed that very poor elimination of ammonia is achieved during a 15-min. period of chlorination in the dark. This result was confirmed by experiments with pure ammonia which will be discussed in the next section. The experiments with pure ammonia had also indicated that ammonia elimination would be favored by avoiding large excesses of chlorine and by operating at pH levels above 6.5.

In Experiments 28 and 29, longer periods of chlorination in the dark were employed. Two samples of a high-ammonia effluent (21 ppm N) were treated in the dark with identical quantities of chlorine while the pH was maintained above 6.5. In Experiment 28, the chlorine was added gradually during 1 hr.; and, in Experiment 29, the chlorine was added all at once. The gradual addition of chlorine produced a greater decrease in ammonia concentration (an 86% decrease compared to a 70% decrease), and less chlorine was required to eliminate a given amount of ammonia. (The amount of chlorine consumed for each ppm of ammonia eliminated was 13.7 ppm for Experiment 28 and 14.9 ppm for Experiment 29.) These differences, although significant, are probably not large enough to warrant the extra effort required to add chlorine gradually.

In subsequent experimental work, after conditions had been established for highly effective oxidation of organic matter in effluents, the rate of oxidation of a low-ammonia effluent was compared with the rate of oxidation of the same effluent when ammonia was added. The effluent used in Experiment 75 (Figure 22, p. 46) was low in ammonia content (1.9 ppm ammonia nitrogen), and the rate of COD elimination (58% after 5 min. of irradiation and 67% after 10 min. of irradiation) was within the range of that observed for other low-ammonia effluents. In Experiment 76 (Figure 25, p. 53), 23 ppm ammonia nitrogen, as ammonium chloride, was added to the effluent. The inhibiting effect on the rate of COD elimination was pronounced; instead of 58% elimination in 5 min., only 4.5% of the COD was eliminated in 5 min.

After about 12 min. in the dark and about 6 min. irradiation, the chlorine concentration had been severely depleted. Therefore, a second addition of chlorine--about equal to the first--was made. This second addition of chlorine evidently was sufficient to overcome the inhibiting effect of the ammonia because a distinct increase in the rate of COD elimination was observed (Figure 25). After a total of 13 min. irradiation, the decrease in COD amounted to 64%. The amount of chlorine required to produce this decrease in COD amounted to 21.6 ppm of chlorine for each ppm of COD; this was almost five times the theoretical amount (4.43 ppm). If the assumption is made that the actual amount of chlorine required to eliminate the COD was equal to the theoretical amount, then the oxidation of 1 ppm of ammonia nitrogen required 17.5 ppm of chlorine; this was almost four times the chlorine demand of 1 ppm of COD.

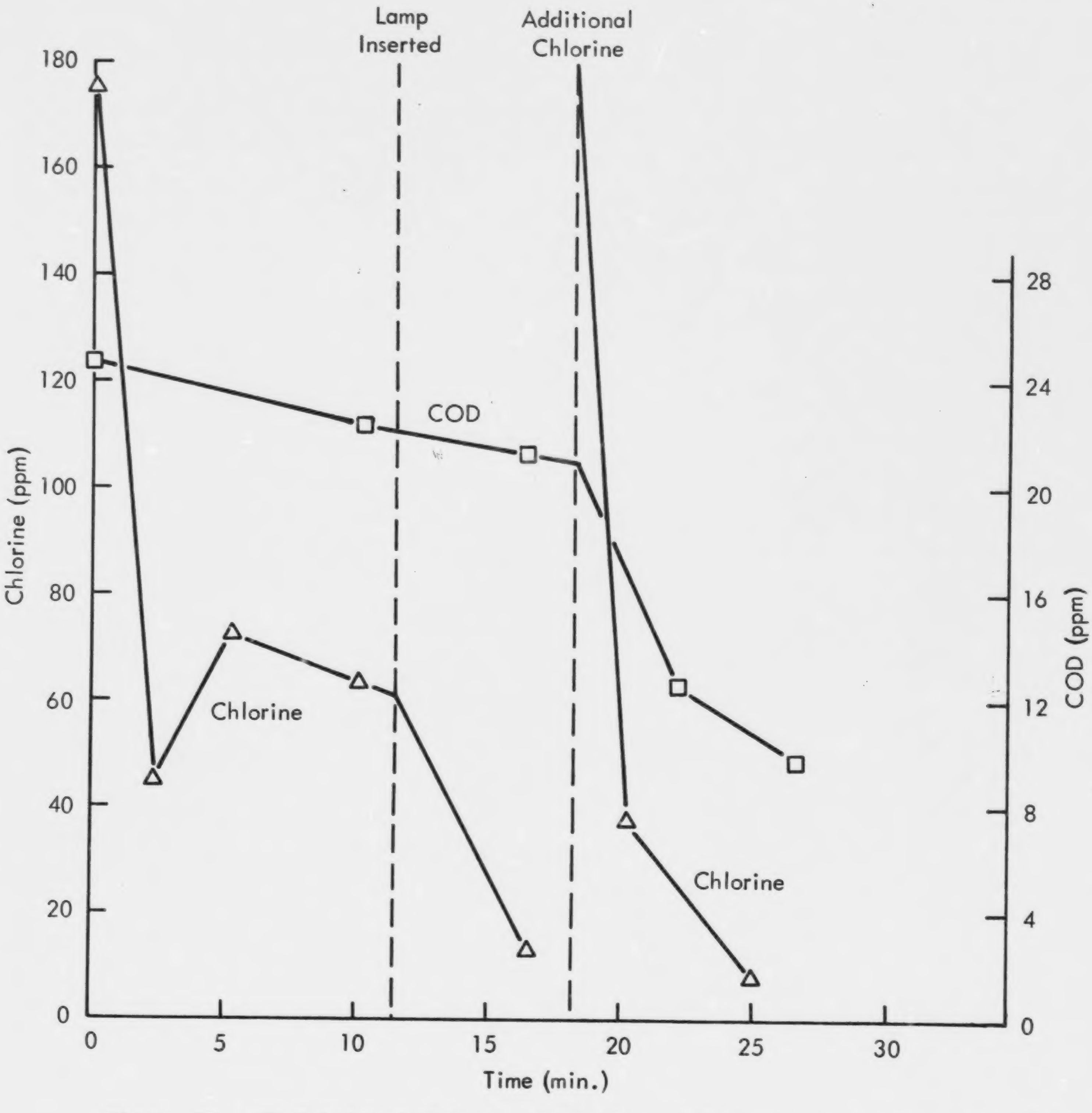

Figure 25 - UV-Catalyzed Chlorine Oxidation of Effluent S&L-624-A Containing 23 ppm of Added Ammonia Nitrogen at pH 5 (Experiment 76)

REACTIONS OF AQUEOUS AMMONIA WITH CHLORINE

Summary

In water, ammonia reacts with chlorine to form mono-, di- and trichloramine in various proportions depending upon pH and ratio of reactants At pH 5, an excess of chlorine rapidly converts most of the ammonia to trichloramine which is relatively stable in the presence of excess chlorine. Irradiation of an ammonia-chlorine reaction mixture rapidly accelerates the conversion of trichloramine to nitrate and other oxidation products of ammonia including, presumably, nitrogen gas.

The Reaction of Aqueous Ammonia with Chlorine

In order to clarify some of the observations made during the studies of high-ammonia effluents, a number of chlorine oxidation experiments were performed using a dilute solution of ammonium chloride.

The general experimental observations are similar to those made with high-ammonia effluents. When chlorine is added to ammonia in the dark, (1) the concentration of chlorine decreases rapidly, (2) the concentration of ammonia decreases rapidly, (3) chloramines are formed rapidly and in varying proportions depending upon pH and reactant ratio, and (4) a slow build-up in nitrate concentration begins. Irradiation of an ammonia-chlorine reaction mixture appears to rapidly accelerate the decomposition of chloramines to products containing nitrogen in higher oxidation states.

A. T. Palin has written a series of three authoritative articles on the ammonia-chlorine interaction in water.[7] Of particular interest to this work are his investigations concerning the products formed from ammonia and chlorine interacting at various pH levels. For example, his studies at pH 5 indicate that, when chlorine (6.0 ppm) interacts with ammonia (0.5 ppm), the solution contains the following products:

	After 10 min.	After 2.0 hr.
Free chlorine	2.7 ppm	2.9 ppm
Trichloramine	0.9 ppm	1.0 ppm
Dichloramine	3.0 ppm	0.0 ppm
Monochloramine	0.0 ppm	0.0 ppm

Palin observed that monochloramine is fairly stable in the presence of excess ammonia, but is decomposed by excess chlorine.

$$2NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_2O$$

He also observed that dichloramine will decompose to nitrogen, HCl and chlorine, but that a solution of trichloramine and excess chlorine is comparatively stable.

Our observations of the ammonia-chlorine reaction in the dark are consistent with these observations, even though our experiments were performed at higher concentrations.

In all of our ammonia-chlorine experiments, rapid and large initial decreases in chlorine concentration were observed (Table XV).

TABLE XV

INITIAL DECREASES IN CHLORINE CONCENTRATION PRODUCED BY AMMONIA

Experiment No.	Initial Ammonia Concn. (ppm N)	Initial Chlorine Concn. (ppm)	Observed Decrease in Chlorine Concentration (ppm)	(min.)
13	12.8	148	105	2.7
17	13.5	408	160	8.5
26	28.8	304	167	2.3

Evidently, this rapid initial reaction is a result of the formation of chloramines, predominantly trichloramine. Chlorine concentrations were determined by the iodide-thiosulfate procedure; and, using this method, only a small proportion of trichloramine will titrate as free chlorine.[8]

During the rapid initial reaction, there is some oxidation of ammonia as evidenced by a rapid, but small, development of nitrate concentration in every case.

The initial rapid decrease in chlorine concentration is followed by a very slow decrease in chlorine concentration. In Experiment 17, the initial decrease in chlorine concentration amounted to 160 ppm within 8.5 min.; but 4 days were required for an additional decrease of 119 ppm.

As the second slow decrease in chlorine concentration proceeds, there is a parallel slow increase in nitrate concentration.

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[8] Standard Methods-Water and Wastewater, 12th Ed., 1965, p. 90, American Public Health Association.

Ammonia-chloramine determinations - In all our experiments, ammonia was determined by the direct Nesslerization procedure. However, in Experiment 26, ammonia determinations after 15 min. varied markedly, depending upon the manner in which the sample was treated. When sodium bisulfite was used to remove residual chlorine, only a slight decrease in ammonia concentration was detected (from 28.8 ppm to 24.4 ppm). When residual chlorine was removed by acidification followed by nitrogen purge, the ammonia content had apparently decreased by 68% (to 9.1 ppm).

We believe that the difference between the high ammonia value obtained when one sample was treated with bisulfite and the low value obtained when a duplicate sample was purged with nitrogen represents the amount of ammonia present as chloramines. Thus, at this point of the reaction, the amount of ammonia present as chloramines was approximately 24.4 - 9.1 = 15.3 ppm N. Reduction with bisulfite converted chloramines back to ammonia, but the nitrogen purge caused ammonia nitrogen to be lost from the solution. This ammonia loss could occur as simple volatilization of the chloramines or by partial hydrolysis of the relatively stable trichloramine to mono- and dichloramines which decomposed to nitrogen (and other products).

Effect of irradiation on the ammonia-chlorine reaction - When an ammonia-chlorine solution is irradiated after standing in the dark for about 15 min., there is a very rapid and extensive decrease in the chloramine concentration, a rapid and substantial additional decrease in the ammonia concentration and a rapid increase in the nitrate concentration. In Experiment 26, the results were as shown in Table XVI.

TABLE XVI

EFFECT OF IRRADIATION ON THE AMMONIA-CHLORINE REACTION

	Initial Concentrations	After 15 Min. in the Dark	After 15 Min. Irradiation
Ammonia (ppm N)	28.8	9.1	4.0
Chlorine (ppm)	304	177	36.8
Chloramines (ppm N)	0	15.3[a]	0.6[a]
Nitrate (ppm N)	0	0.25	6.35

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a/ The difference between the high ammonia value obtained when one sample was treated with bisulfite, and the low value obtained when a duplicate sample was purged with nitrogen, provides an approximation of the chloramine concentration.

The results obtained upon irradiation were similar, even after the ammonia-chlorine solution had been allowed to stand for 4 days in the dark (Experiment 17, Table XVII).

TABLE XVII

EFFECT OF IRRADIATION ON AN AMMONIA-CHLORINE SOLUTION THAT HAD BEEN ALLOWED TO STAND IN THE DARK FOR 4 DAYS

	Initial Concentrations	After 4 Days in the Dark	After 30 Min. Irradiation
Ammonia (ppm N)	13.5	1.6	0
Chlorine (ppm)	408	229	0
Nitrate (ppm N)	0.02	4.0	9.0

These results indicate that chloramines are very rapidly decomposed by UV radiation to products other than ammonia. Nitrate appears to be the major product, but other oxidation products of ammonia are also formed.

COMPARISON OF UV RADIATION SOURCES

Summary

At the present time, mercury-arc lamps are probably the most practical sources of UV radiation for the catalytic chlorine oxidation of organic material in wastewater. On the basis of organic oxidation rate produced per watt of UV output, high-pressure mercury arcs, which emit a broad spectrum of wavelengths (220 - 366 mμ), are about 2.7 times more efficient than low-pressure mercury arcs which emit almost exclusively at one wavelength (253.7 mμ).

A Comparison of UV Radiation Sources

Lewis R. Koller in his text, *Ultraviolet Radiation*,[9] discusses in considerable detail the various sources of UV radiation. Other than sunlight, the two most-useful UV sources are arcs and incandescent materials. The most efficient and most useful of these are the arcs. For a number of practical reasons, mercury arcs have been the most-widely-used UV sources. In our opinion, mercury-arc lamps are, at the present time, the most practical source of UV radiation for use in the catalyzed chlorine oxidation process.

There are basically two kinds of mercury-arc lamps: the high-pressure arc and the low-pressure arc.

The source of ultraviolet radiation in all of our experiments thus far described has been a high-pressure mercury-arc lamp. Lamps of this kind emit a broad spectrum of wavelengths between 220 mμ and 366 mμ. (For a description of this spectrum, see Figure 26). Low-pressure, mercury-arc lamps emit radiation almost exclusively at 253.7 mμ. High-pressure mercury arcs generally emit much-more-intense radiation than low-pressure mercury arcs of about the same size. However, the useful life of high-pressure lamps is usually much shorter, and the cost of high-pressure lamps is considerably greater, than that of low-pressure lamps of the same size. Also, low-pressure lamps convert electrical energy to radiant energy more efficiently. A disadvantage of the low-pressure lamps is that the 253.7-mμ-wavelength is not transmitted by water or wastewater to the extent that longer wavelengths are. All these factors--intensity, wavelength, catalytic efficiency, lamp cost, lamp life, and electrical efficiency--must be considered in determining the most useful, UV source for the catalytic chlorine oxidation.

The catalytic efficiency of radiation from low-pressure lamps in promoting the catalytic oxidation was unknown, and could only be determined experimentally.

The low-pressure lamp which we used was manufactured by the Nester/Faust Manufacturing Corporation and is probably the most intense, short-wavelength source available commercially which will fit in the photochemical reactor. The electrical output and electrical efficiency characteristics of this lamp are compared with those of the high-pressure lamp in Table XVIII.

TABLE XVIII

COMPARISON OF LABORATORY-SCALE, MERCURY-ARC LAMPS

	High-Pressure Lamp[a]	Low-Pressure Lamp[b]
Input	450 w.	50 w.
UV output	83.7 w.	40 w.
Electrical efficiency	18.6%	80%

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a/ These figures were obtained from Hanovia Lamp Division, Engelhard Hanovia, Inc., Research Laboratory Bulletin, 5-1-59.

b/ These figures were supplied by Mr. Conman of Nester/Faust Manufacturing Corporation.

Using the low-pressure lamp, effluent oxidation experiments were conducted at pH 5 and at pH 10; and the same effluent was treated in the same manner using the high-pressure source. The results of these experiments (Experiments 55-57) are presented in Figures 27-29.

As expected, the rate of the oxidation is greater at pH 5 (Figure 27) than at pH 10 (Figure 29); COD was eliminated about three times faster at pH 5 than at pH 10, and TOC was eliminated more than seven times faster at pH 5 than at pH 10.

The difference in organic oxidation rate produced by the two sources was also about as expected. A comparison of Figure 27 with Figure 28 shows that the less-intense low-pressure lamp produces COD elimination and TOC elimination at about a fivefold slower rate than the high-pressure lamp.

The efficiency of chlorine utilization was about the same in each of these experiments: the low-pressure lamp produced a COD elimination of 0.122 ppm for each ppm of chlorine consumed; the high-pressure lamp produced a COD elimination of 0.126 ppm for each ppm of chlorine consumed.

Although the high-pressure lamp produces a fivefold greater oxidation rate, its catalytic efficiency--expressed as the rate of COD elimination per watt of UV output--is not five times as great as that of the low-pressure lamp. The rate of COD removal produced by the low-pressure source was 0.447 ppm/min; the rate of COD removal produced by the high-pressure source was 2.51 ppm/min. Dividing these rates by UV output of each lamp (40 w. for the low-pressure lamp; 83.7 w. for the high-pressure lamp) yields a figure which represents the catalytic efficiency of COD elimination based on radiant energy (Table XIX).

TABLE XIX

CATALYTIC EFFICIENCY OF COD ELIMINATION BASED ON RADIANT ENERGY

Low-Pressure Lamp	0.0112 ppm/min/watt of UV output
High-Pressure Lamp	0.0300 ppm/min/watt of UV output

Thus, the high-pressure mercury arc produces COD elimination more than five times faster than the low-pressure arc, and the catalytic efficiency of the high-pressure radiation is about 2.7 times greater than radiation from the low-pressure arc.

Overall process costs for both kinds of lamps have been estimated based on this information, and are presented in a separate section of this report. (See "Process Costs", p. 80)

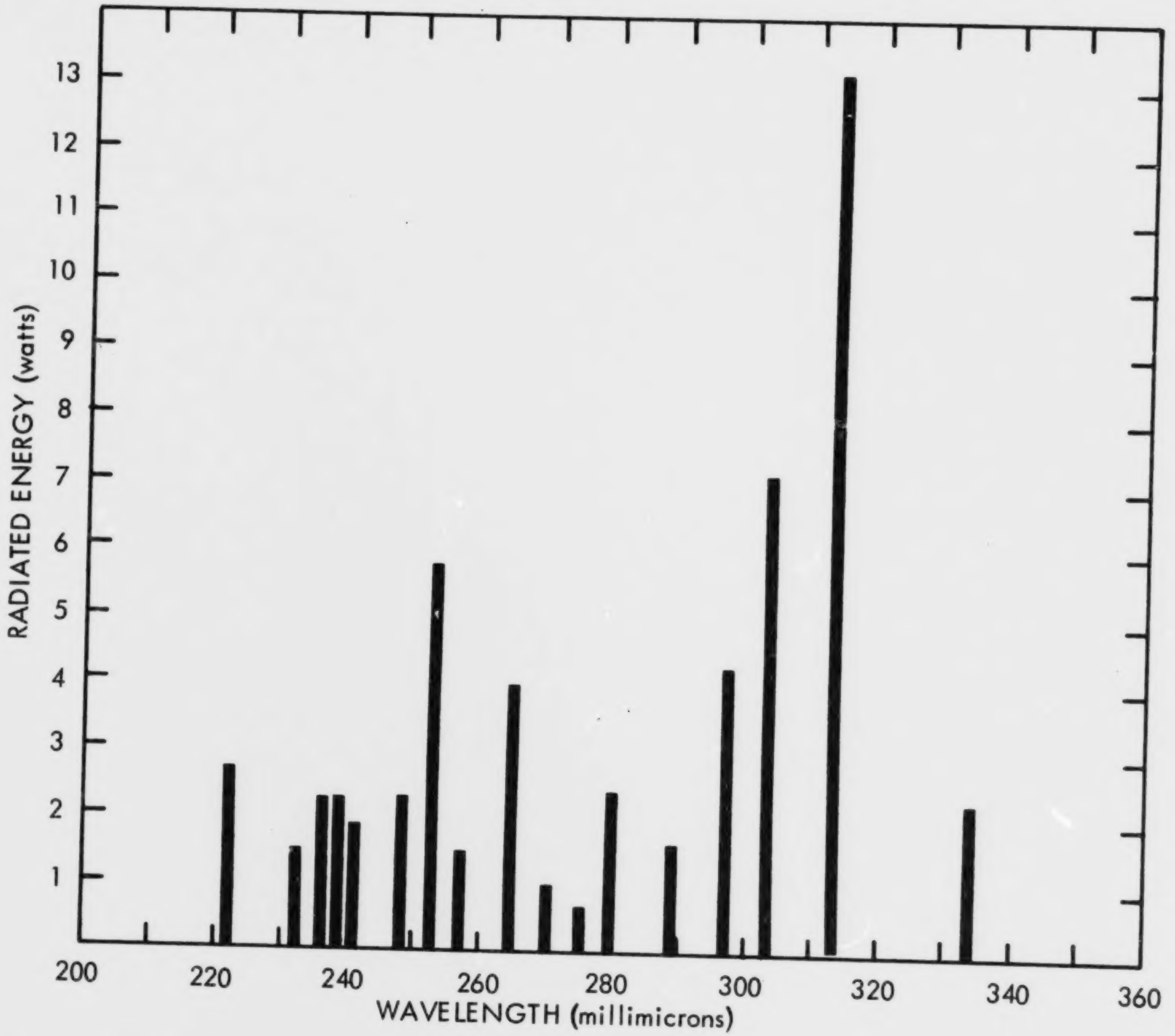

Figure 26 - Ultraviolet Spectral Energy Distribution of the Emission from a 450-w., Quartz, Mercury-Vapor Lamp (Excluding the 25.6-w. Line at 366 mμ)

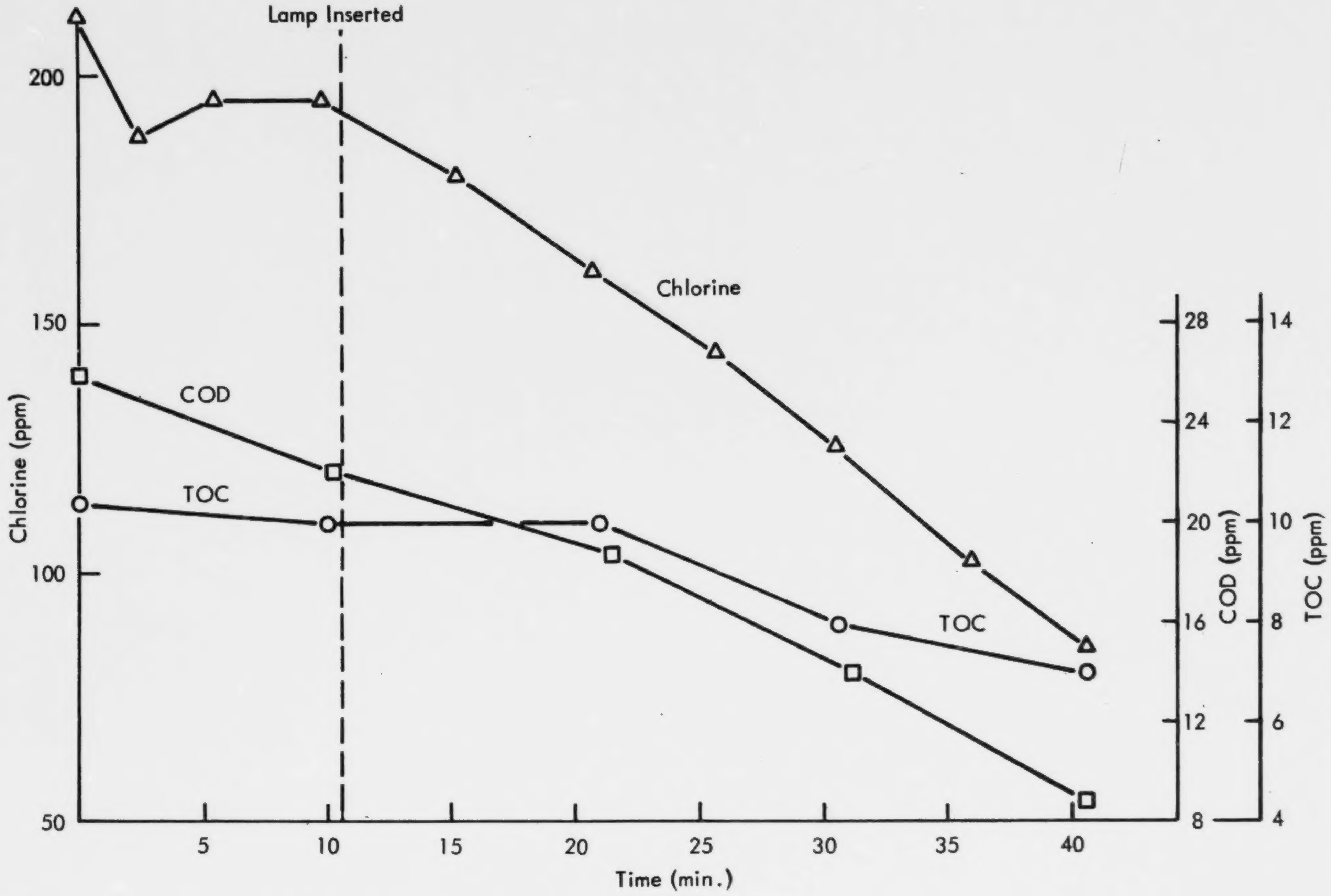

Figure 27 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-516 at pH 5 Using a Low-Pressure UV Source (Experiment 55)

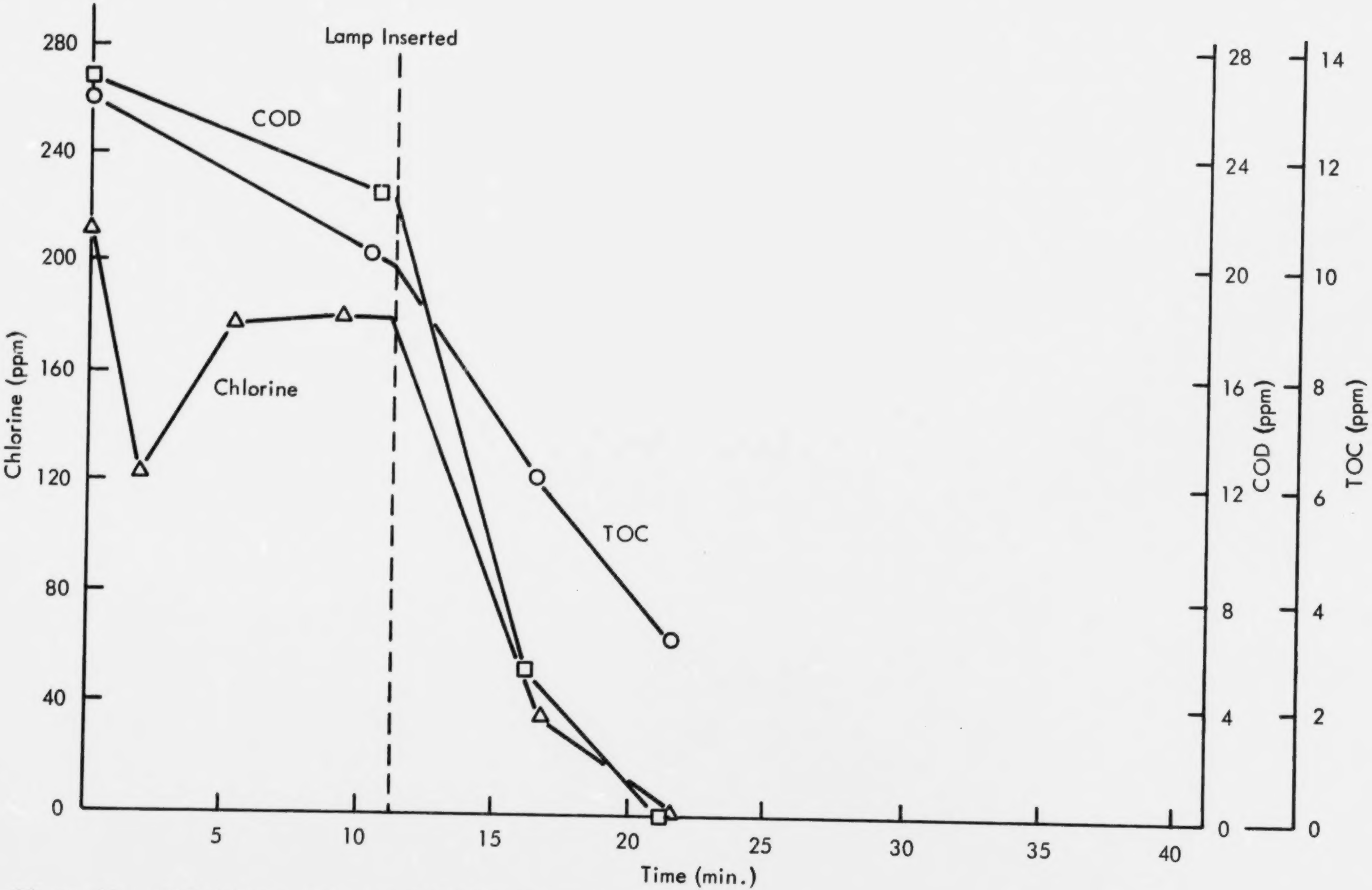

Figure 28 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-516 at pH 5 Using the High-Pressure UV Source (Experiment

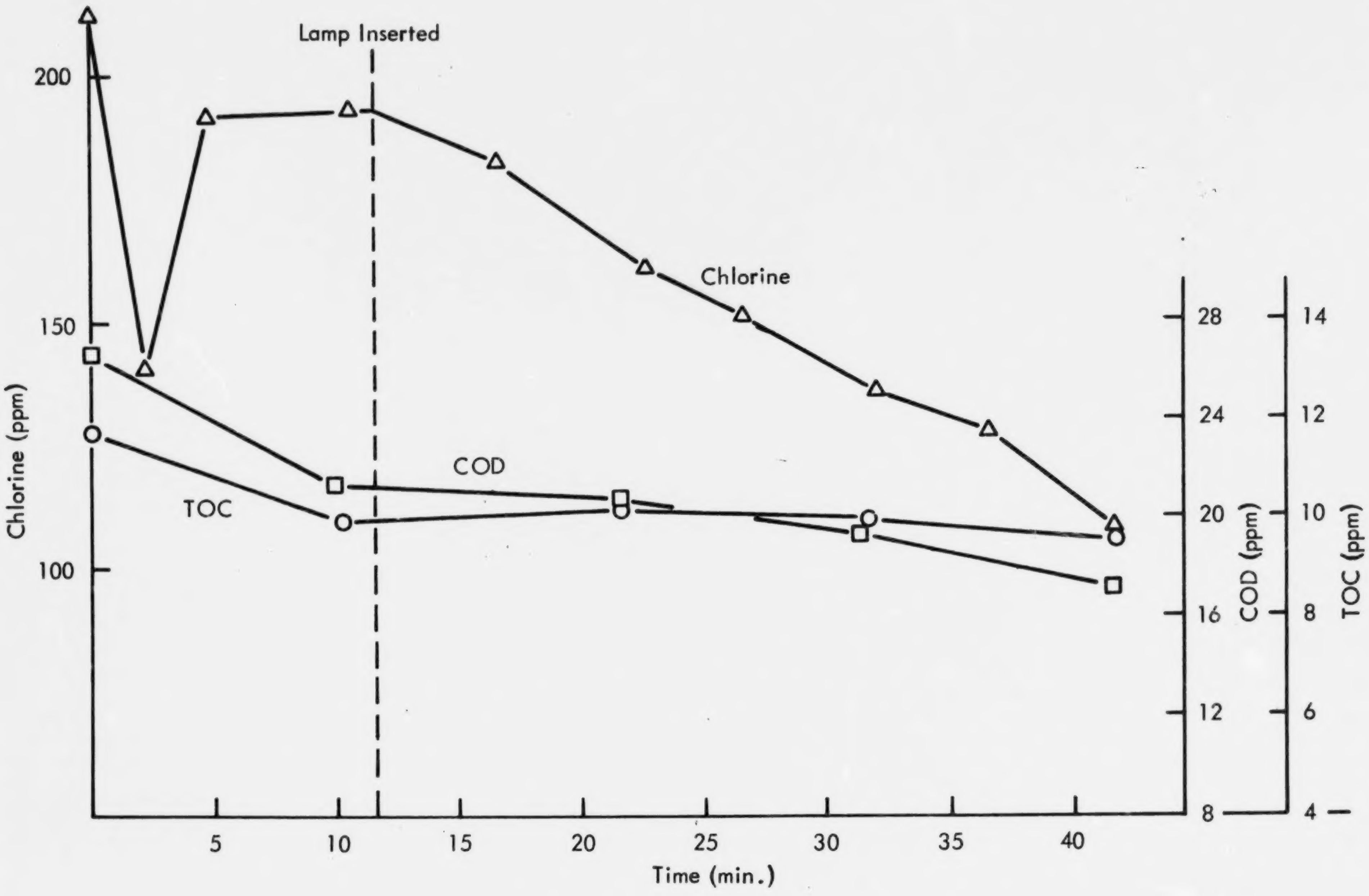

Figure 29 - UV-Catalyzed Chlorine Oxidation of Effluent MRI-516 at pH 10 Using a Low-Pressure UV Source (Experiment 57)

ULTRAVIOLET-CATALYZED CHLORINE OXIDATION OF PURE COMPOUNDS

Summary

A brief investigation was made of the effect of UV-catalyzed chlorine oxidation on the TOC of water containing eight pure organic compounds. The following compounds are oxidized rapidly and extensively: phenol (61%, 8 min.), 2,4-dinitrophenol (53%, 10 min.), glycine (61%, 4 min.), formic acid (90%, 4 min.), and *o*-dinitrobenzene (65%, 10 min.). Benzoic acid is also oxidized (45%, 10 min.), but not as fast as the other compounds. Acetic acid and ethanol are oxidized at a much slower rate (less than 10%, 10 min.)

Ultraviolet-Catalyzed Chlorine Oxidation of Pure Compounds

In order to provide information concerning the types of chemical compounds that can be oxidized by the UV-catalyzed chlorine oxidation, eight pure compounds were subjected to conditions approximating those of the effluent oxidation experiments.

The oxidation of pure organic compounds was of low priority and of secondary interest during the present research contract. Therefore, these experiments were designed so that they could be performed rapidly and with only a minimum of analytical work.

Only the rate and extent of compound destruction were measured, usually by TOC determinations or ultraviolet spectra analyses; and no attempt was made to determine the number or kinds of products formed. In all of these experiments, the pH was maintained near 5.0; this was the pH range found to be optimum in the effluent oxidation studies.*

Phenol - The rate of oxidation of phenol was followed by means of TOC analyses (Figure 30) and appears to be quite rapid (61% after 8 min. of irradiation). The rate of TOC elimination appears to level off after about 61% of the TOC has been eliminated, but this decrease in rate may have been caused by the depletion of chlorine.

2,4-Dinitrophenol - Also shown in Figure 30 are the results of the 2,4-dinitrophenol oxidation. The rate of oxidation of this compound is also very rapid, as indicated by the rapid decrease in ultraviolet absorbance at 256 mμ (practically 100% elimination in 8 min.) and the fairly rapid decrease in TOC (53% in 10 min.).

Acetic acid - Acetic acid is apparently not oxidized rapidly under these conditions (Figure 31). The results of the TOC analyses are somewhat erratic, probably because of loss of volatile organics during the oxygen-gas purge of the sample prior to TOC determination. However, the results are sufficiently conclusive to indicate that no large decrease in TOC occurred during the 10-min. period of irradiation. Chemical oxygen demand (COD) analyses were also made on samples from this reaction. The COD results indicate that only about 29% of the COD was eliminated during the 10-min. period of irradiation. However, the results of the COD analyses are lower than the theoretical values because acetic acid is not completely oxidized by dichromate during the COD determinations.

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* There is no reason to believe that pH 5 would be the optimum pH for the oxidation of every kind of organic compound.

Our COD analytical prodecure calls for 50 ml. of sample. The refluxing mixture of sample and acidic dichromate is concentrated by allowing 25 ml. of distillate to accumulate in a Dean Stark Trap. In the COD determinations, the first acetic acid sample was analyzed in triplicate; and in one of the determinations, the distillate was submitted for TOC determination. A comparison of the TOC value (10.6 mg/liter) of the distillate with that of the starting material (14.2 mg/liter) shows that 37% of the acetic acid collects in the distillate receiver during the COD determinations.

The procedure of concentrating a large COD sample is recommended by Standard Methods[10/] for dilute samples, even though the unavoidable loss of volatile acids is recognized.

In spite of the analytical difficulties, it may be concluded that only a relatively small fraction of the acetic acid was oxidized by the UV-catalyzed chlorine oxidation.

Ethanol - The TOC data from the ethanol oxidation experiment (Experiment 62, Figure 31) indicate that the oxidation of ethanol does not proceed to a very great extent in 10 min. (Again there appear to be inaccuracies in the TOC data, probably because of loss of volatile products prior to the determination.) Probably the alcohol is oxidized rapidly by the UV-catalyzed reaction to acetic acid (no loss in TOC) which is subsequently oxidized at a much lower rate. The more rapid decrease of chlorine concentration in the ethanol oxidation (compared to the acetic acid oxidation, Experiment 61, Figure 31) is an indication that the ethanol was being at least partially oxidized.

Triplicate COD determinations were made on the original ethanol sample; and, as in the acetic acid determinations, a significant (18%) loss of volatile material from the refluxing COD mixture was detected.

Glycine - The oxidation of glycine is apparently quite rapid compared to acetic acid. The observed TOC decrease amounted to 61% in 4 min. (Figure 32), but the rate of TOC decrease appeared to level off after it had decreased by about 78%. We have no explanation for the apparent temporary decrease in TOC which occurred in the dark.

Benzoic acid - The oxidation of benzoic acid proceeds at a fairly rapid rate according to the TOC figures: 45% in 10 min. (Figure 33). This oxidation of benzoic acid does not occur in the dark since no significant consumption of chlorine nor decrease in TOC occurred during a 10-min. period of chlorination in the dark.

Formic acid - Formic acid is very rapidly oxidized by the UV-catalyzed reaction (Figure 34). The extent of TOC decrease amounted to 90% within 4 min. Practically no oxidation occurred during an initial 10-min. period of chlorination in the dark. It is not difficult to explain why a 10% residual of TOC was not eliminated. TOC values of 1.2-1.4 mg/liter are not significantly different from zero; and, therefore, the actual amount of TOC elimination achieved was perhaps 100%.

o-Dinitrobenzene - The rate and extent to which *o*-dinitrobenzene can be oxidized came as a surprise (Figure 35). The extent of oxidation was followed both by UV absorbance and by TOC determinations. Both analytical techniques indicated that rapid and extensive oxidation occurred upon irradiation. Almost all the chlorine had been consumed after 10 min. irradiation; and the TOC decrease amounted to 19% in 5 min., 65% in 10 min. and 73% in 15 min. At the end of 16 min., practically all the UV absorbance at 255 mμ had been eliminated. However, the actual time required for this elimination was probably much less than 16 min. because only a relatively small amount of oxidation is required to destroy the aromatic ring which is predominantly responsible for the UV absorbance.

In the dark, no significant oxidation occurred during 10 min.; as determined in a separate experiment (Experiment 74), UV radiation in the absence of chlorine produces no decrease in absorbance during 20 min. radiation.

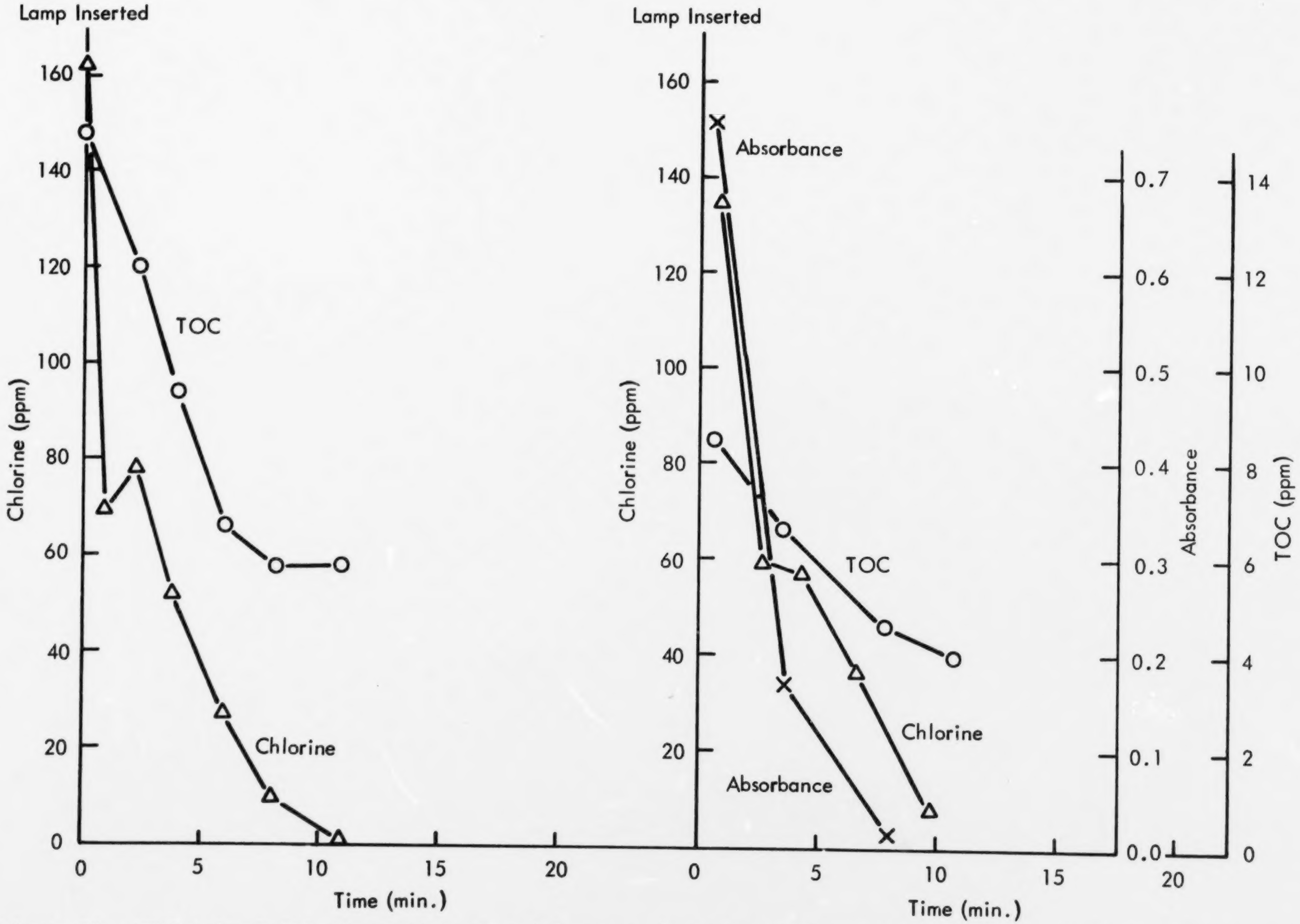

Figure 30 - UV-Catalyzed Chlorine Oxidation of (a) Phenol (Experiment 60) and (b) 2,4-Dinitrophenol (Experiment 63)

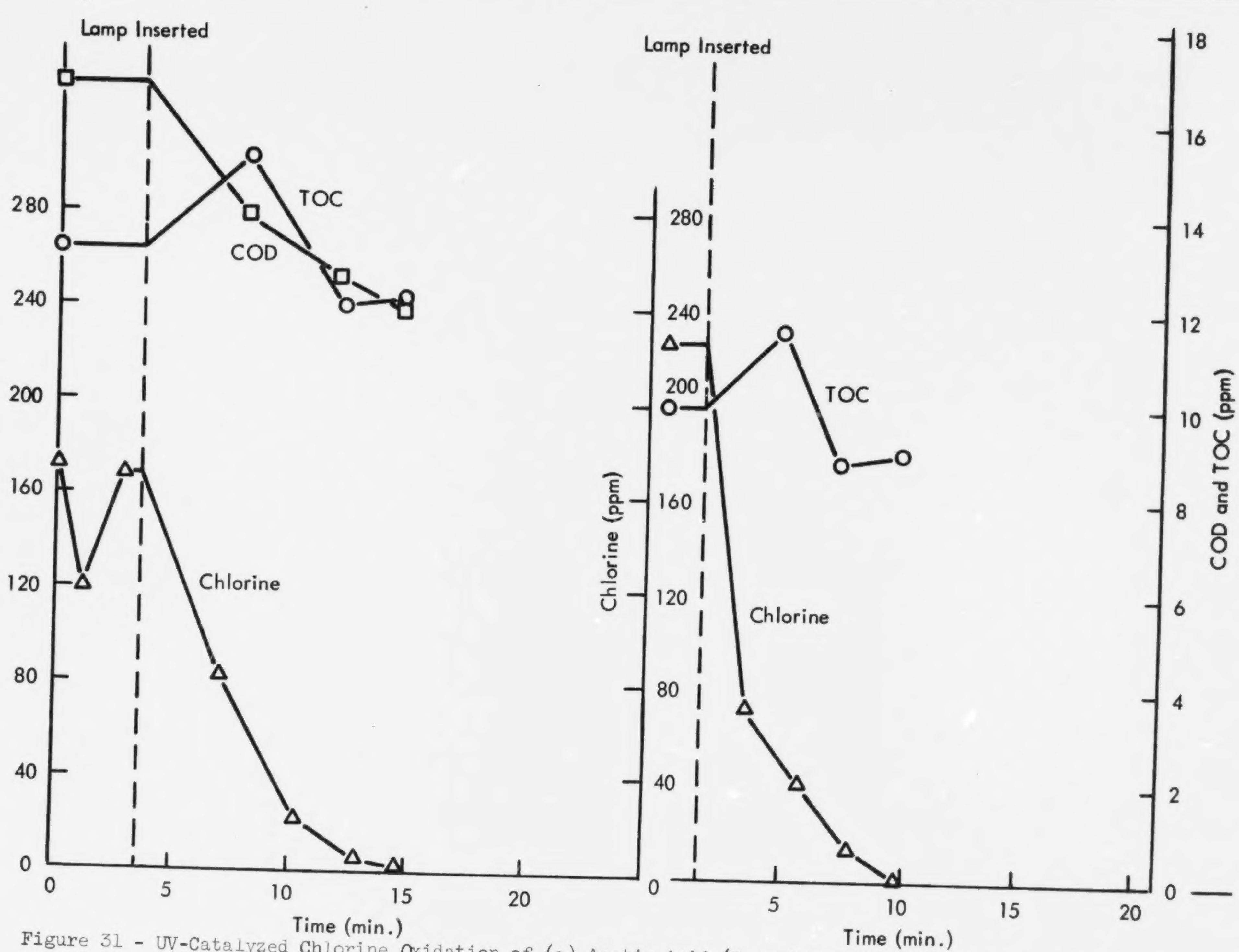

Figure 31 - UV-Catalyzed Chlorine Oxidation of (a) Acetic Acid (Experiment 61) and (b) Ethanol (Experiment 62)

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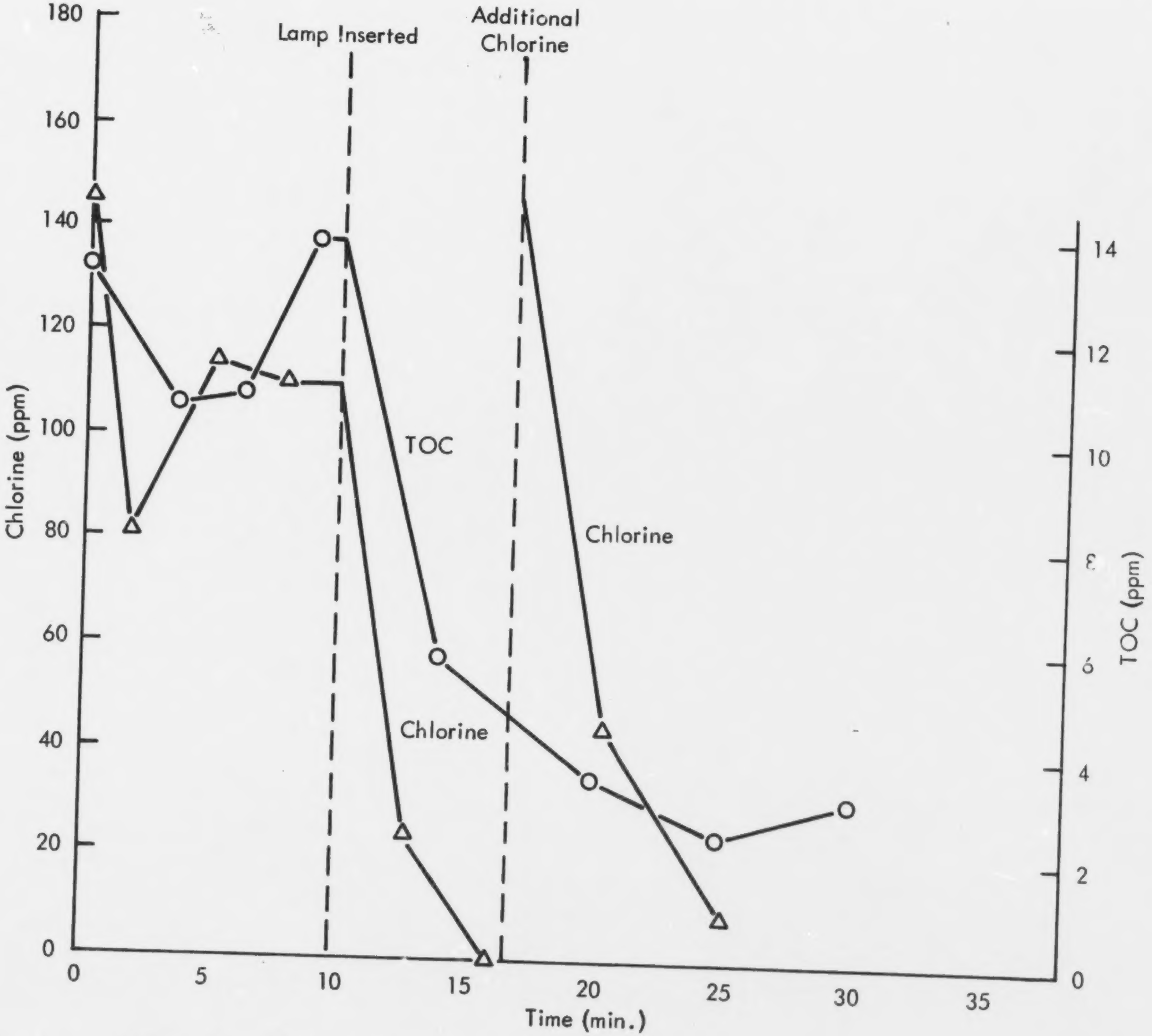

Figure 32 - UV-Catalyzed Chlorine Oxidation of Glycine (Experiment 68)

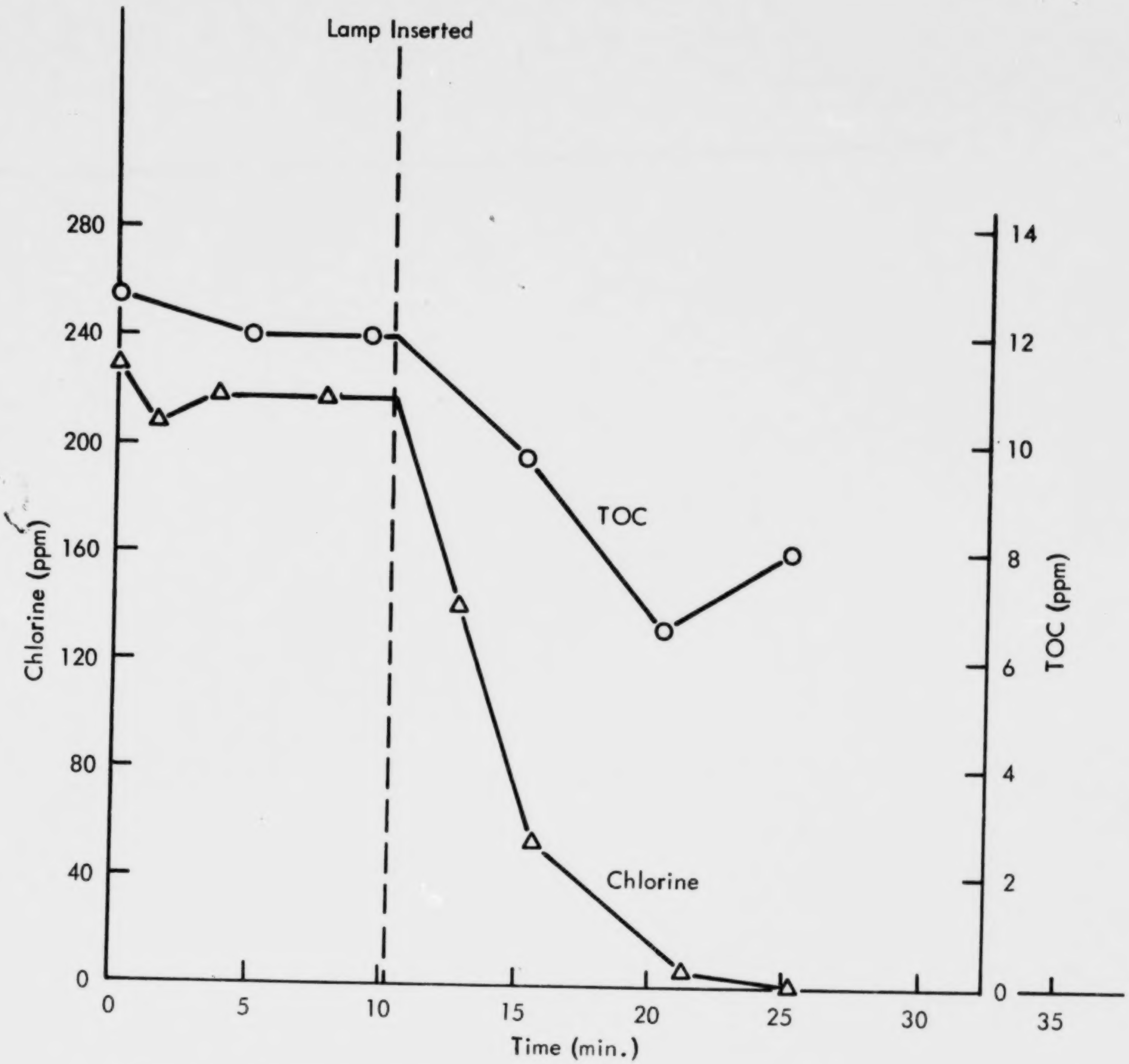

Figure 33 - UV-Catalyzed Chlorine Oxidation of Benzoic Acid (Experiment 69)

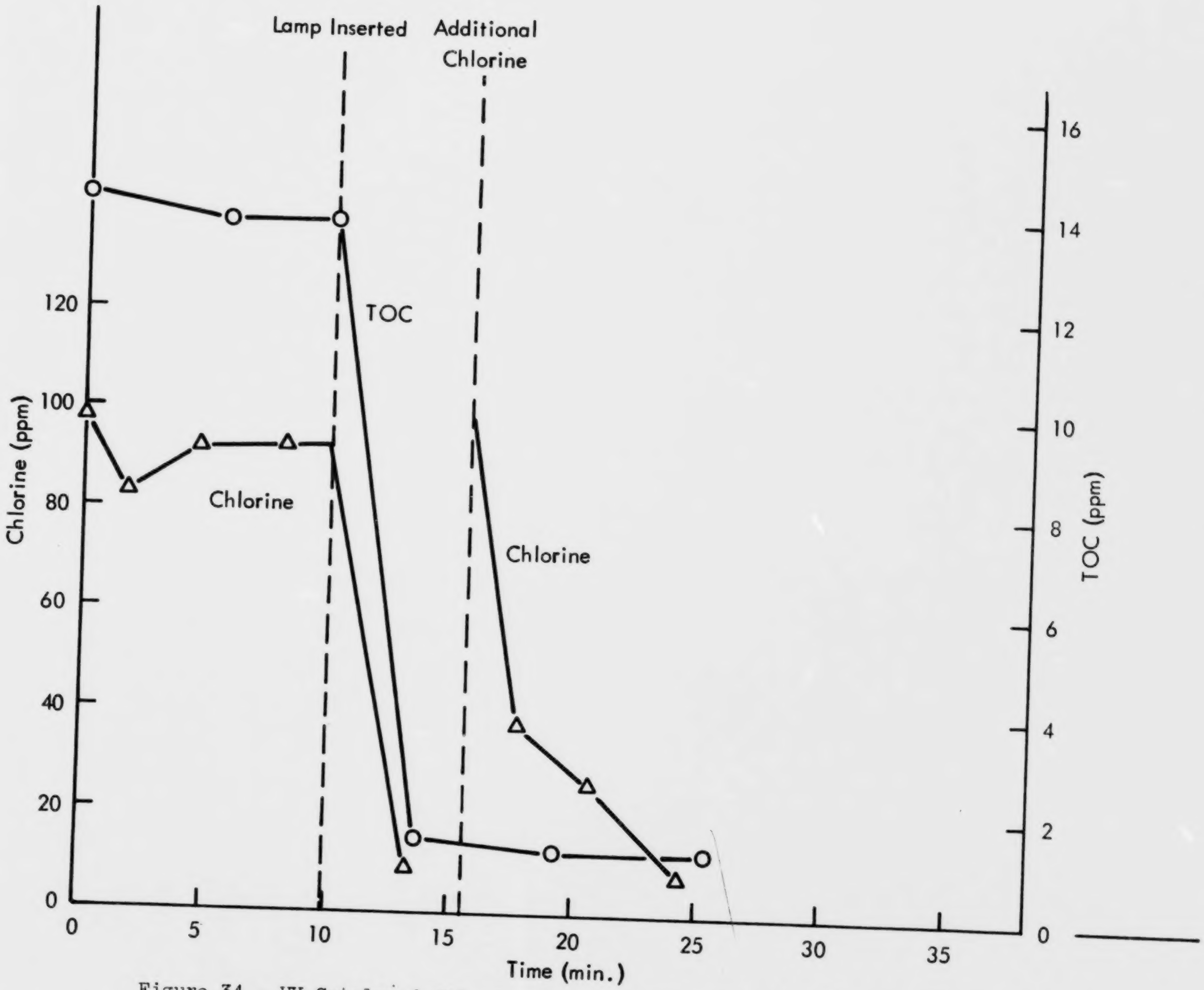

Figure 34 - UV-Catalyzed Chlorine Oxidation of Formic Acid (Experiment 70)

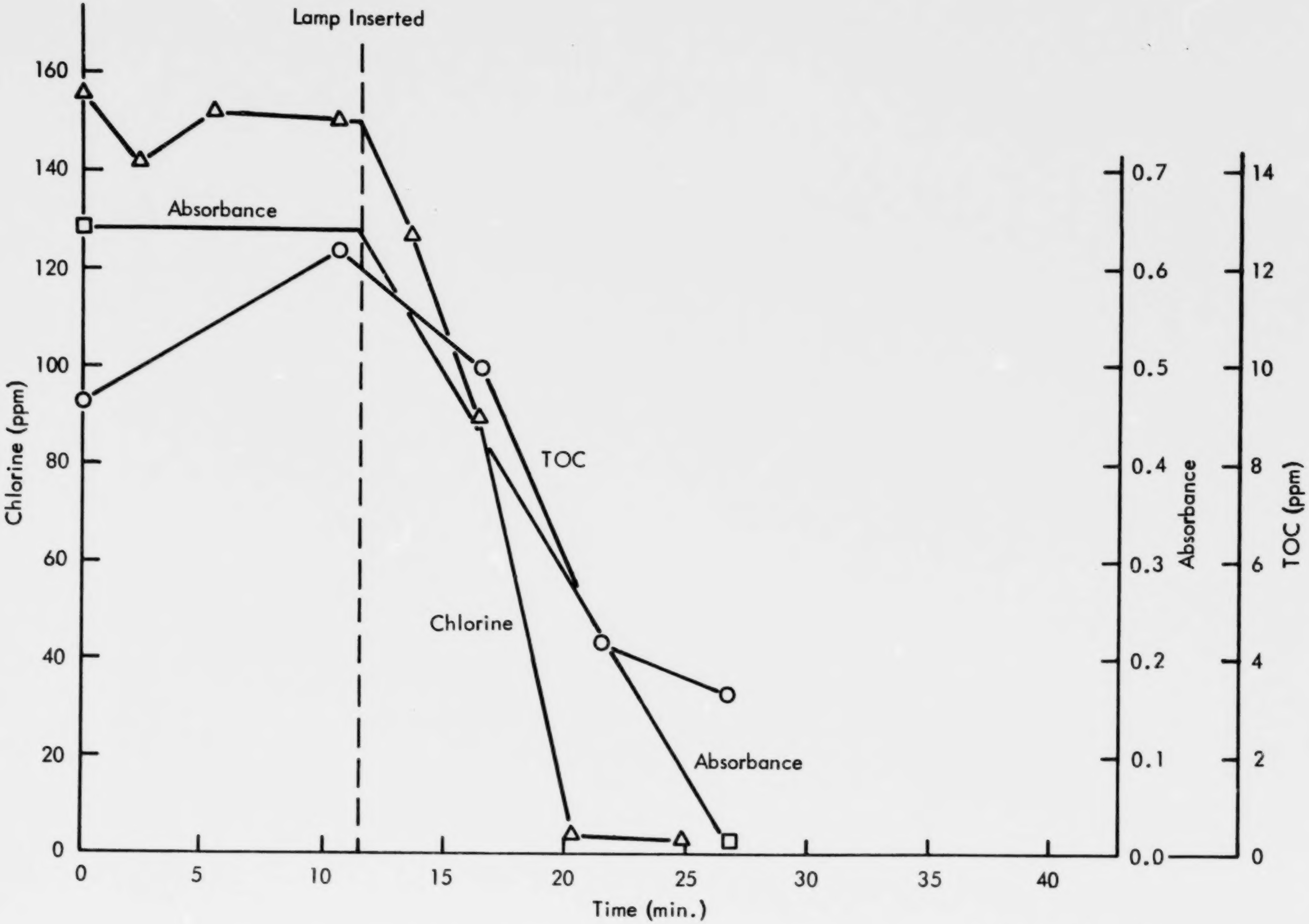

Figure 35 - UV-Catalyzed Chlorine Oxidation of o-Dinitrobenzene (Experiment 73)

INVESTIGATION OF THE EFFECT OF ULTRAVIOLET RADIATION PLUS OTHER OXIDIZING AGENTS

Summary

A very brief study was made of the extent of organic oxidation produced when wastewater was treated with UV radiation plus (1) molecular oxygen, and (2) hydrogen peroxide. No significant reduction in TOC was detected after oxygen had been bubbled through an irradiated reaction mixture for 20 min. Hydrogen peroxide produced no significant decrease in TOC after 30 min. in the dark; irradiation of this reaction mixture for another 30 min. produced only a slight decrease in TOC.

Investigation of the Effect of Ultraviolet Radiation, Plus Other Oxidizing Agents

Two reagents, oxygen and hydrogen peroxide, were investigated for the purpose of determining whether or not the oxidizing action of these reagents could be accelerated by UV radiation. Both reagents are possible intermediates in UV-catalyzed chlorine oxidation. Therefore, the purpose of these experiments was to provide results useful for the interpretation of UV-catalyzed chlorine oxidation, as well as to explore possibilities for novel UV-catalyzed oxidations.

Because of the relatively low priority of these experiments, no elaborate analytical studies were made.

Treatment of wastewater with oxygen and UV radiation - In Experiment 80, pure oxygen gas was continuously bubbled through an effluent while the reaction mixture was irradiated. (No adjustment of pH was made prior to, or during, the experiment.) The results of this experiment were compared with a similar experiment in which nitrogen gas was bubbled through the irradiated reaction mixture. In neither experiment was there a significant decrease in TOC in 20 min.

UV radiation alone had no detectable effect on the TOC content of this effluent within a period of 45 min. In prior experiments, UV-catalyzed chlorine oxidation of this effluent had produced large decreases in both TOC and COD (Experiments 75, 77, 78; Figures 19, 21, 22; pp. 43, 45, 46).

The results of these experiments showed conclusively that (1) molecular oxygen cannot be an intermediate in the UV-catalyzed chlorine oxidation, and (2) UV radiation plus oxygen do not produce much organic oxidation compared to UV radiation plus chlorine.

Treatment of wastewater with hydrogen peroxide and UV radition - The same effluent used in the above series of experiments was treated in the dark with hydrogen peroxide in excess of the amount required to oxidize all the organic material in the effluent to CO_2 (Figure 36). After 30 min. in the dark, no significant decrease in TOC was observed, and there was only a slight decrease in the hydrogen peroxide concentration. The reaction mixture was then irradiated for 30 min. The irradiation produced only a very slight acceleration in the rate of decrease in hydrogen peroxide concentration. There was also a small (20%) decrease in TOC during the 30-min. irradiation period.

The results of this experiment indicated that (1) hydrogen peroxide cannot be an intermediate in the UV-catalyzed chlorine oxidation, and (2) hydrogen peroxide plus UV radiation produces only a slight amount of effluent oxidation compared to UV radiation plus chlorine.

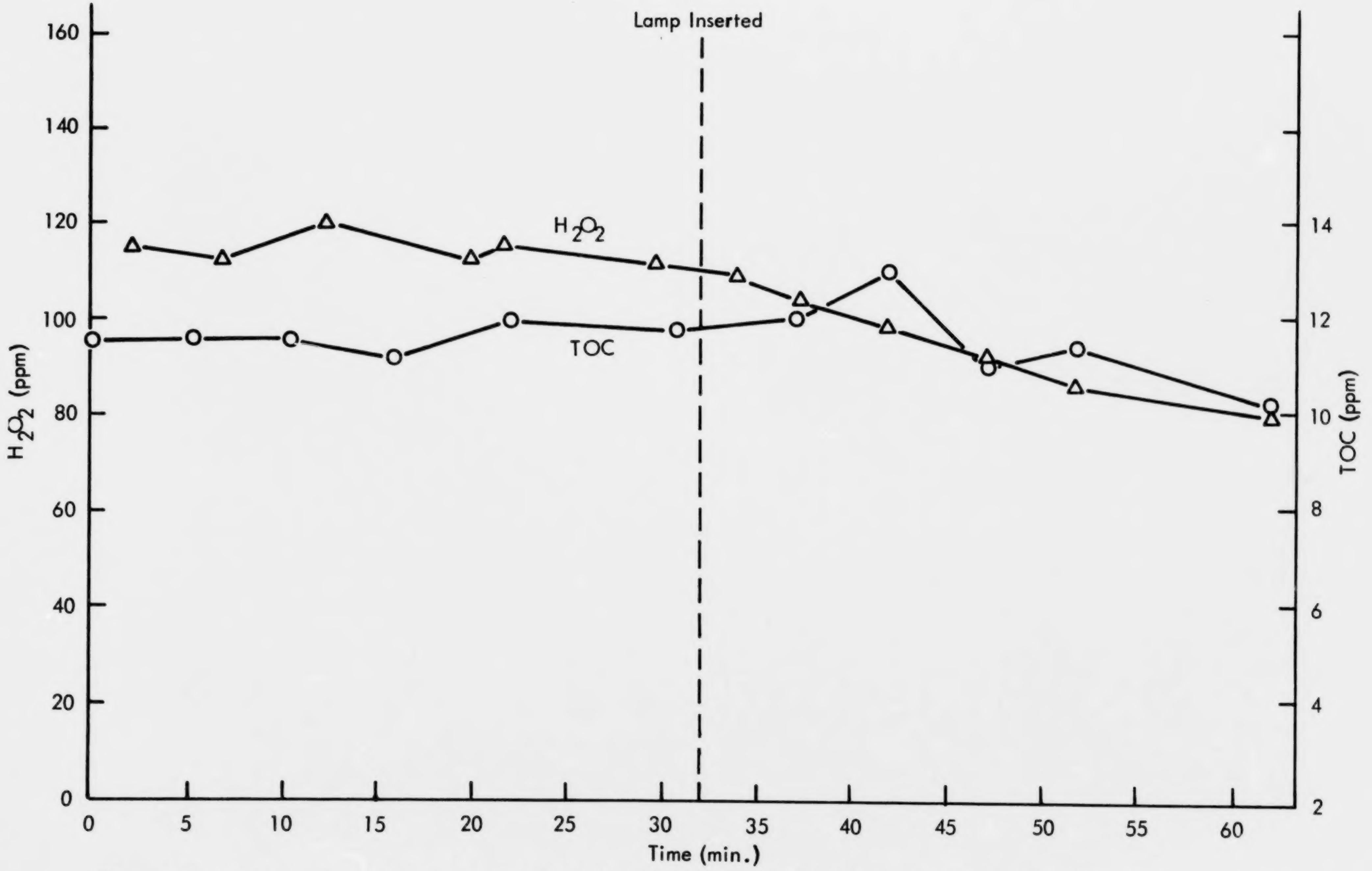

Figure 36 - Treatment of Effluent S&L-624 With Hydrogen Peroxide and Ultraviolet Radiation (Experiment 81)

PROCESS COSTS

Summary

Preliminary, process-cost estimates were made for the application of the UV-catalyzed chlorine oxidation to the treatment of wastewater on a large scale. Costs of 7.2¢ to 11.1¢/1,000 gal. were estimated for a plant producing 10-million gal/day. Because of the nature of this process, costs would not increase significantly for plants producing 1-million gal/day.

In determining process costs, the major factors considered were (1) the commercial availability of UV-radiation sources, (2) the design and efficiency of the reactor system, (3) the transmission of UV radiation by wastewater, and (4) the costs of chlorine, lamps, power and structure.

The assumptions made were that a contact time of 10 min. is required for effective organic oxidation and that the catalytic process requires the application of 15 times more radiant energy than that required for UV sterilization.

Process costs could be lowered substantially if any one of the following factors could be reduced: (1) the amount of radiant energy per unit volume required for effective oxidation, (2) the contact time, and (3) the cost of the radiation source. The precise determination of these factors can only be achieved by a study designed to determine exactly how much wastewater can be treated effectively using each radiant energy source.

Process Costs

There are four important factors to consider in estimating the cost of UV-catalyzed chlorine oxidation on a large scale. These are (1) the cost of chlorine, (2) the cost of the ultraviolet lamps, (3) the power cost, and (4) the cost of structure which includes land, labor, maintenance, capital, and interest charges.

The cost of chlorine is the only simple factor to calculate. Assuming that the average, highly nitrified (less than 4 ppm NH_3) effluent will possess a COD of 30 ppm, the theoretical amount of chlorine which must be applied is 133 ppm. The application of 135 ppm of chlorine will cost 4.10¢/1,000 gal. (taking the price of chlorine as 3.65¢/lb).[11/]

As will be subsequently shown, all the other costs are directly related to the amount of water which can be treated by an individual UV lamp.

Commercially available, ultraviolet sources - Earlier in this report, the opinion was stated that mercury-arc lamps are--at the present time--the most practical source of UV radiation for this application. Two types of mercury-arc lamps were also discussed earlier. (Both of these topics are discussed in the section concerning UV sources, p. 59.) Some characteristics of several, commercially available, UV lamps are shown in Tables XX and XXI.

These lamps represent only a small fraction of the mercury-arc lamps that are commercially available and were selected to provide representative examples.

The ideal lamp for this process may not be presently available commercially. Most of the lamps that are available were evidently designed for specific uses. Perhaps a special lamp design could be devised which would provide the particular characteristics (e.g., long life, intense output of highly effective wavelengths, etc.) which would be best suited to this process. Perhaps cheaper lamps, similar to those used for visual illumination purposes, could be employed with no large offsetting decrease in reaction-promoting efficiency. However, a consideration of the lamps described in Tables XX and XXI will permit an estimate of the lamp costs which would be encountered in large-scale processes using currently available, mercury-arc lamps.

General design considerations - In determining process costs, the most difficult factor to estimate is the amount of water which can be treated with a given amount of UV energy. Obviously, a given volume and type of water will require the application of a certain specific amount of UV energy for a certain specific time in order to achieve a pre-determined, product-water quality.

TABLE XX

COMMERCIALLY AVAILABLE, MERCURY-ARC LAMPS[a]

Lamp (G. E. Ordering Abbreviation)	Type[b]	Length (in.)	Electrical Input (watts)	UV Output (watts)	Life (hr.)
UA-11	HP	22	1,200	255	1,000
UA-37	HP	52	3,000	782	1,000
G64T6	LP	64	65	18.5	7,500
G36T6	LP	36	35	13.7	7,500
G30T8	LP	36	30	8.8	7,500
H1500-A23	MP	12	1,500	486	6,000
H 400-A33-1	FL	2[c]	400	22	24,000

---

a/ The data in this table were obtained from General Electric.

b/ HP = High pressure, LP = Low pressure, MP = Medium pressure, FL = Floodlamp

c/ The arc length of this lamp is about 2 in.; however, the lamp itself is about 8 in. long.

TABLE XXI

SPECTRAL ENERGY DISTRIBUTION (IN WATTS) OF SELECTED MERCURY-ARC LAMPS[a]

Lamp (G. E. Ordering Abbreviation)	Type[b]	Far UV (220-280 mμ)	Middle UV (280-320 mμ)	Near UV (320-400 mμ)	Visible (400-700 mμ)
UA-37	HP	250(22%)	279(25%)	252(22%)	347(31%)
G64T6	LP	18(90%)	0.4(2%)	0.3(1.5%)	1.3(6.5%)
H1500-A23	MP	189(26%)	157(22%)	140(20%)	227(32%)
H 400-A33-1	FL	0(0%)	1.5(2%)	20.5(26%)	55.7(72%)

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a/ The data in this table were obtained from General Electric.

b/ HP = High pressure, LP = Low pressure, MP = Medium pressure, FL = Floodlamp

TABLE XXII

REPLACEMENT COSTS OF MERCURY-ARC LAMPS[a]

Lamp (G. E. Ordering Abbreviation)	Lamp Cost[b] ($)	Daily Cost[c] ($)	Daily Cost of 100 Watts of UV Output ($)
UA-11	97	2.33	0.914
UA-37	147	3.68	0.470
G64T6	14	0.0448	0.242
G36T6	12.5	0.0400	0.292
G30T8	3.5	0.0112	0.128
H1500-A23	112.5	0.450	0.0927
H 400-A33-1	12.4	0.0124	0.0564

---

a/ The data in this table were obtained from General Electric.

b/ These figures are the replacement costs of the individual lamps if the lamps are purchased in large quantities.

c/ The daily cost is the replacement cost divided by the lamp life in days.

The General Electric brochure on germicidal lamps (TP-122) states that a device, such as the one shown in Figure 37, "will provide 90% disinfection (with a 100% factor of safety) of drinkable water, transmitting 2537 Å effectively to a depth of at least 5 in., if these rates of flow are not exceeded: (lamp) G-30T8, 500 gallons per hr." In this apparatus, the amount of water treated at one time is 36 x 5 x 8 = 1440 in^3 = 6.24 gal. At a flow rate of 500 gal/hr, the average "contact time" is 0.748 min., and the UV energy applied is 1.06 w.-min/gal.*

Our studies have indicated that a contact time of approximately 10 min. will be required for substantial elimination of COD and TOC. A 10-min. contact time in a reactor such as the one described in Figure 37 would reduce the flow rate to 37.4 gal/hr, and the UV energy applied would be 14.1 w.-min/gal. Therefore, in our cost estimation, we have assumed that effective organic removal can be achieved by the application of 15 w.-min/gal.

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* The G-30T8 lamp emits 8.8 w. of UV energy (8.8 x 0.748) ÷ 6.64 = 1.06 w. min/gal.

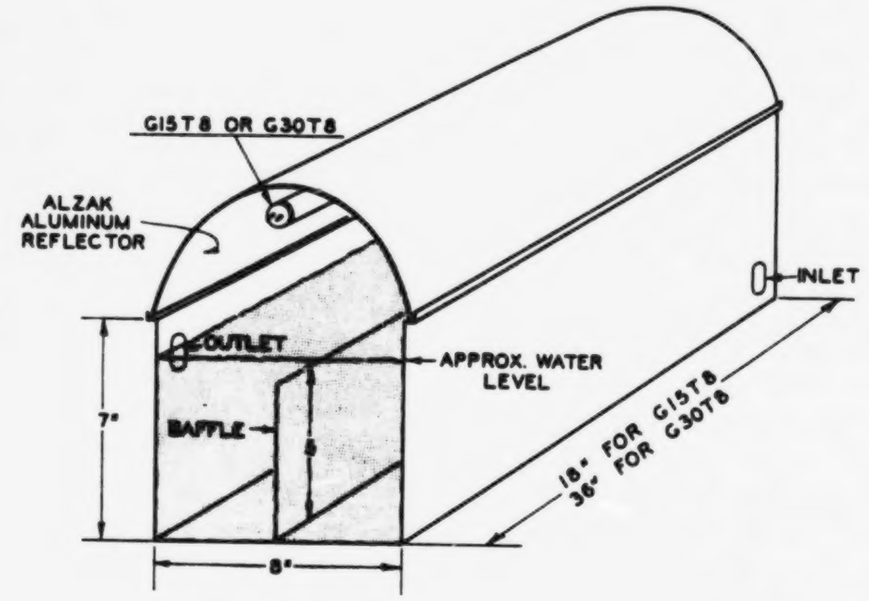
G15T8 OR G30T8
ALZAK ALUMINUM REFLECTOR
INLET
OUTLET
APPROX. WATER LEVEL
7"
BAFFLE
5
8"
18" FOR G15T8
36" FOR G30T8

Figure 37 - Suggested Dimensions and Ratings of a Small, Gravity-Type Water Disinfector*

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* This is the simplest of four designs proposed by General Electric in their brochure on Germicidal Lamps (TP-122). The designations G15T8 and G30T8 refer to lamps produced by GE.

Transmission of UV radiation by wastewater - Another factor which will influence the amount of water which can be treated at one time is the UV transmission characteristics of the water. The General Electric Company has used the term "Effective depth of penetration" (EDP) which is the depth at which 90% of the UV energy has been absorbed. This value is simple to determine for a single wavelength such as that used in germicidal applications, and it varies from 2 to 5 in. for a typical wastewater.* However, for high-pressure, mercury-arc irradiation the EDP is more difficult to determine because of the spectrum of wavelengths emitted by these lamps. Since most of the energy emitted by high-pressure lamps is of longer wavelength, a considerable increase in EDP would be expected. For example, examination of the UV spectrum of a typical wastewater shows that the EDP at 366 mμ (the most prominent wavelength emitted from a high-pressure mercury arc) is at least six times as great as the EDP at 253.7 mμ. *Furthermore, our studies have shown that, as the UV-catalyzed chlorine oxidation proceeds, the UV transmission of the wastewater increases greatly* (see Experimental, p. 118).

In germicidal operations, the EDP cannot be exceeded without decreasing the effectiveness of the process. However, the UV-catalyzed oxidation process is not subject to this limitation. In germicidal operations, it is required that no portion of the water receive less than a sterilizing dose of radiation. However, in the oxidation process, even the smallest amount of UV energy will contribute to the extent of oxidation. In germicidal operations, UV energy must be wasted to insure sterilization; in the oxidation process, maximum utilization of UV energy is desired. Thus, for maximum efficiency, the oxidation process must treat water at depths which substantially exceed the EDP for sterilization applications.

Cost of lamps, power and structure - The above discussion indicates that many factors must be considered in selecting the most effective, UV source and reactor design for large-scale water treatment. However, based upon the assumption that 15 w.-min/gal of UV energy will be required for the catalyzed chlorine oxidation, some estimates of the cost of presently available lamps, power, and structure can be made.

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* Personal communication, Dr. R. B. Dean, Cincinnati Water Research Laboratory.

Lamp costs - The UA-37 lamp (Tables XX and XXI) is representative of high-pressure mercury arcs. The 782-w. UV output of this lamp would permit the treatment of 52.2 gal/min., or 75,100 gal/day. Considering the daily lamp replacement cost of \$3.68 (Table XXI), the lamp cost would be 4.90¢/gal.

Our laboratory studies have shown that the catalytic efficiency of high-pressure lamps is 2.7 times greater than that of the low-pressure lamps (Table XIX). Therefore, for performance comparable to that of the high-pressure lamps (which are assumed to be capable of operating effectively with an application of 15.0 w.-min/gal), the amount of energy required from low-pressure lamps would have to be 40.0 w.-min/gal.

The G64T6 lamp (Tables XX and XXI) is typical of low-pressure mercury arcs. This lamp emits only 18.5 w. of UV energy which would permit the treatment of only 0.46 gal/min, or 665 gal/day. Considering the daily replacement cost (Table XXI), the lamp cost would amount to 6.74¢/1,000 gal.

The relatively high costs of both types of these lamps suggest that other radiation sources be considered. Since the relative efficiency of longer wavelengths is not known, perhaps cheaper lamps which provide irradiation in the near ultraviolet (340-400 mμ) or short-wavelength visible (400-450 mμ) might be developed especially for this application.

Two other types of mercury-arc lamps are described in Tables XX through XXII. One of these is a 1,500 w. medium-pressure lamp (G. E. ordering abbreviation H1500-A23) and the other is a 400 w. mercury-arc lamp for floodlighting applications (G. E. ordering abbreviation H400-A33-1). These lamps have been designed to provide exceptionally long lifetimes. The longer life of these lamps plus the fact that they are marketed in large volume, results in significantly lower daily costs per 100 w. of UV output (Table XXII).

Power costs - The high-pressure lamp (UA-37) requires 3,000 w. of input electrical energy. The daily cost of this energy would be 57.6¢/lamp, assuming that power costs 0.80¢/kw-hr. Since our calculations indicate that each lamp will treat 75,100 gal/day, power cost would be 0.77¢/1,000 gal. of water treated.

The low-pressure lamp (G64T6) requires only 65 w. of input electrical energy, or a daily cost per lamp of 1.25¢. Assuming that each lamp treats 1,400 gal/day, the power cost would be 0.89¢/1,000 gal.

On a similar basis, power cuts for the medium-pressure lamp (H1500-A23) would be 0.62¢/1,000 gal.; for the floodlamp (H400-A33-1), 0.35¢/1,000 gal.

Structure costs - If each high-pressure lamp (UA-37) will treat 75,100 gal. of water per day, then 133 lamps are required for a plant processing 10-million gal/day. The size of this plant can be estimated at 2,310 sq. ft., based on the length of the lamps and by assuming that the total width required for the channel is 4 ft. At $10/sq. ft., the estimated cost of structure would be $23,100. Straight-line depreciation (20 years) places the daily contribution of structure cost at $3.21. Maintenance (at 1½% of structure cost) is estimated at 36¢/day. The daily labor cost (one man, 24 hr/day) of $120/day would be the most significant factor in structure cost.

Thus, for the high-pressure lamps, the total cost of structure, land, maintenance, labor, capital and interest is estimated at $125/day, or 1.25¢/1,000 gal.

Structure costs are considerably higher for the low-pressure lamps because of the greater number of lamps required. Each low-pressure lamp (G64T6) will presumably treat 665 gal. of water per day. This means that 15,000 lamps are required for a 10-million gal/day plant. In order to hold the size of the plant to a reasonable figure, we have assumed that five lamps can be used in each unit cell. We have further assumed that no loss of radiant energy is produced by this grouping of the lamps. Making the same assumptions as were made for the high-pressure lamps, a plant size of 30,600 sq. ft. and costing $306,000 is obtained. Straight-line depreciation (20 years) leads to a daily structure cost of $42.50. Maintenance would be $4.67, and labor (two men, 24 hr/day) is estimated at $240/day.

Thus, for the low-pressure lamps, the total cost of structure, land, labor, capital, and interest is estimated at $290/day, or 2.90¢/1,000 gal.

Structure costs cannot be estimated on a similar basis for the medium-pressure lamp or the floodlamp because of their considerably shorter arc-lengths. However, using the above estimates and assuming that structure costs will be inversely proportional to the amount of water treated per lamp, the structure cost for the medium-pressure lamp would be 1.50¢/1,000 gal., structure cost for the floodlamp would be 2.70¢/1,000 gal.

Total process costs - Total estimated process costs are shown in Table XXIII. Process costs for the high-pressure and low-pressure lamps are approximately the same, and there is an obvious "trade-off" between these two kinds of lamps; the low-pressure lamps are cheaper, but require higher structure costs.

Total process costs for the medium-pressure (H1500-A23) and floodlamp (H400-A33-1) are significantly lower because of the lower cost of producing ultraviolet energy using these lamps.

Each of these estimated total process costs could be lowered considerably if any one of the following factors could be reduced: (1) the amount of radiant energy per unit volume required for effective oxidation, (2) the contact time, and (3) the cost of the radiation source. The precise determination of these factors can only be achieved by a study designed to determine exactly how much wastewater can be treated effectively using each radiant energy source.

TABLE XXIII

ESTIMATED PROCESS COSTS[a] (CENTS/1,000 GAL)

	High-Pressure Lamps	Low-Pressure Lamps	Medium-Pressure Lamps	Floodlamp
Chlorine	4.10	4.10	4.10	4.10
Lamps	4.90	3.20	0.97	0.59
Power	0.77	0.89	0.62	0.36
Structure	1.25	2.90	1.50	2.70
	11.02	11.09	7.19	7.75

---

[a] Costs were calculated assuming: (1) that a contact time of 10 min. was required; (2) that the ultraviolet energy required is 15.0 w.-min/gal. for the high-pressure lamps and 40.0 w.-min/gal. for the low-pressure lamps; and (3) that the low-pressure lamps could be operated in clusters of five with no significant loss in radiant energy.

EXPERIMENTAL

Photochemical Reactor

All of the effluent oxidation experiments were performed in the photochemical reactor shown in Figure 38. The reactor consisted of a typical laboratory apparatus for the investigation of UV-catalyzed reactions and was suitably equipped to permit thermal control, rapid sampling, continuous monitoring of pH and the addition of aqueous alkali to control pH as the oxidation proceeded. The reactor vessel was a 5-liter, four-necked flask equipped with a quartz immersion well. The immersion well (Hanovia Lamp Division, Engelhard Hanovia, Inc.) contained the ultraviolet source, and was equipped with an outer jacket through which cooling water was circulated. This well was located in the large center neck of the flask.

A combination pH electrode was placed in one of the side-necks. Into another side-neck was placed a thermometer, thermocouple well, and a glass tube which led to a syringe-type sampling device (Manostat Corporation). The third side-neck was equipped with a 500-ml., pressure-equalizing, addition funnel.

The contents of the flask were stirred by a magnetic stirrer. Temperature was controlled by a "Gardsman" controller (West Instrument Corporation) which was activated by the thermocouple. The controller activated an off-on switch which regulated the flow of cooling water to the immersion well. A regulator was used to maintain the pressure of the cooling water at about 5 psi. If additional cooling was required, the cooling water was passed through a coil of aluminum tubing immersed in ice-water. Reactions "in the dark" were performed by wrapping the reactor in aluminum foil.

Ultraviolet Radiation Sources

The ultraviolet source for almost all the oxidation experiments was a 450-w., high-pressure, mercury-vapor lamp powered by a 285-v. transformer (radiated energy, 175.8 w.). The lamp and transformer are products of the Hanovia Lamp Division, Engelhard Hanovia, Inc. The spectral output of this lamp is typical of high-pressure, mercury-arc lamps and is shown in detail in Table XXIV and graphically in Figure 26 (p. 63).

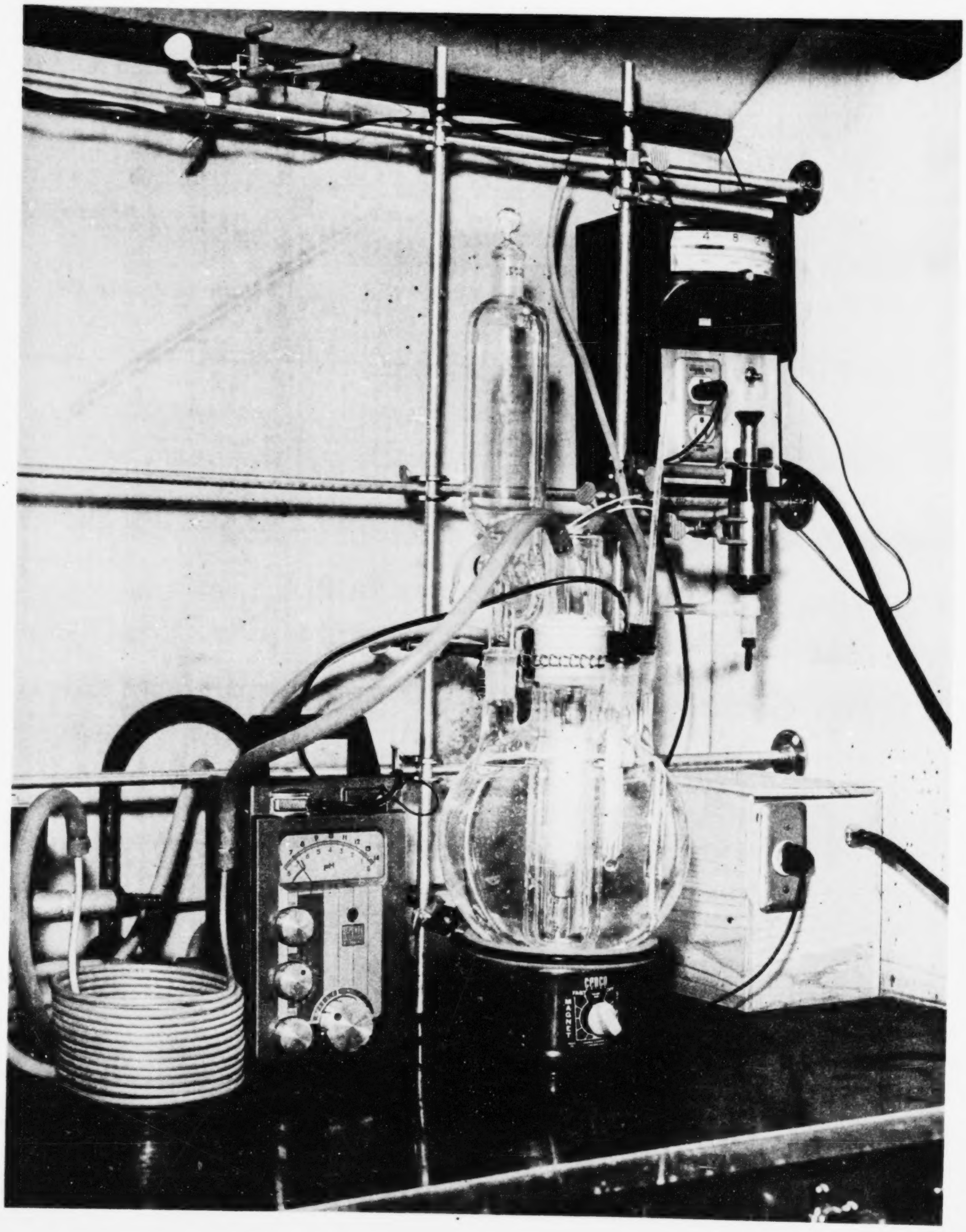

Figure 38 - Reactor for UV-Catalyzed Chlorine Oxidations

TABLE XXIV

SPECTRAL-ENERGY DISTRIBUTION OF HIGH-PRESSURE, MERCURY-ARC LAMP

Mercury Lines (millimicrons)	Radiated Energy (watts)
1367.3 (infrared)	2.6
1128.7	3.3
1014.0	10.5
578.0 (yellow)	20.0
546.1 (green)	24.5
435.8 (blue)	20.2
404.5 (violet)	11.0
366.0 (UV)	25.6
334.1	2.4
313.0	13.2
302.5	7.2
296.7	4.3
289.4	1.6
280.4	2.4
275.3	0.7
270.0	1.0
265.2	4.0
257.1	1.5
253.7 (reversed)*	5.8
248.2	2.3
240.0	1.9
238.0	2.3
236.0	2.3
232.0	1.5
222.4	3.7
Total watts	175.8

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* 253.7 line is reversed in high-pressure lamps.

An alternate ultraviolet source was a low-pressure, mercury-arc lamp manufactured by Nester/Faust Manufacturing Corporation and specially modified to fit in our reactor. This lamp was selected because it is probably the most intense, short-wavelength source available commercially which would fit within the immersion well. The electrical output and electrical efficiency characteristics of this lamp are compared with those of the high-pressure lamp in Table XVIII (p. 61). Data supplied by the manufacturer indicated that 96% of the UV output of this lamp is between 245 mμ and 260 mμ.

Analytical Methods

All analytical determinations were performed as described in Standard Methods.12/ Total organic carbon (TOC) determinations were performed at the Cincinnati Water Research Laboratory by means of a Beckman carbonaceous analyzer; the brucine method was used for nitrate determinations; ammonia was determined by direct Nesslerization; chlorine was determined using the iodometric procedure. All analytical samples were immediately acidified to pH 1 with concentrated sulfuric acid in order to stabilize the samples for COD and TOC analyses.

The acidified (pH 1) samples for COD analysis were dechlorinated by purging the sample with nitrogen gas until no chlorine could be detected by means of starch-iodide paper. The removal of chlorine by this method is facilitated by low pH values (Figure 39), and this step usually required about 15-20 min. Longer periods of time were required when the effluent contained more than 4 ppm of ammonia. The TOC sample was dechlorinated with excess, solid, sodium bisulfite, and was similarly acidified.

Sources of Wastewater

The primary sources of wastewater were local, municipal, sewage-treatment plants of the extended aeration type. Another source of wastewater was an experimental sewage-treatment plant operated by the Smith & Loveless Corporation, Lenexa, Kansas. This plant is also of the extended aeration type and treats sewage from the city of Lenexa, Kansas. Apparently, the design of this plant is to be patented, and the company cannot release details of the process. The Smith & Loveless plant proved to be a very reliable source of highly nitrified effluent.

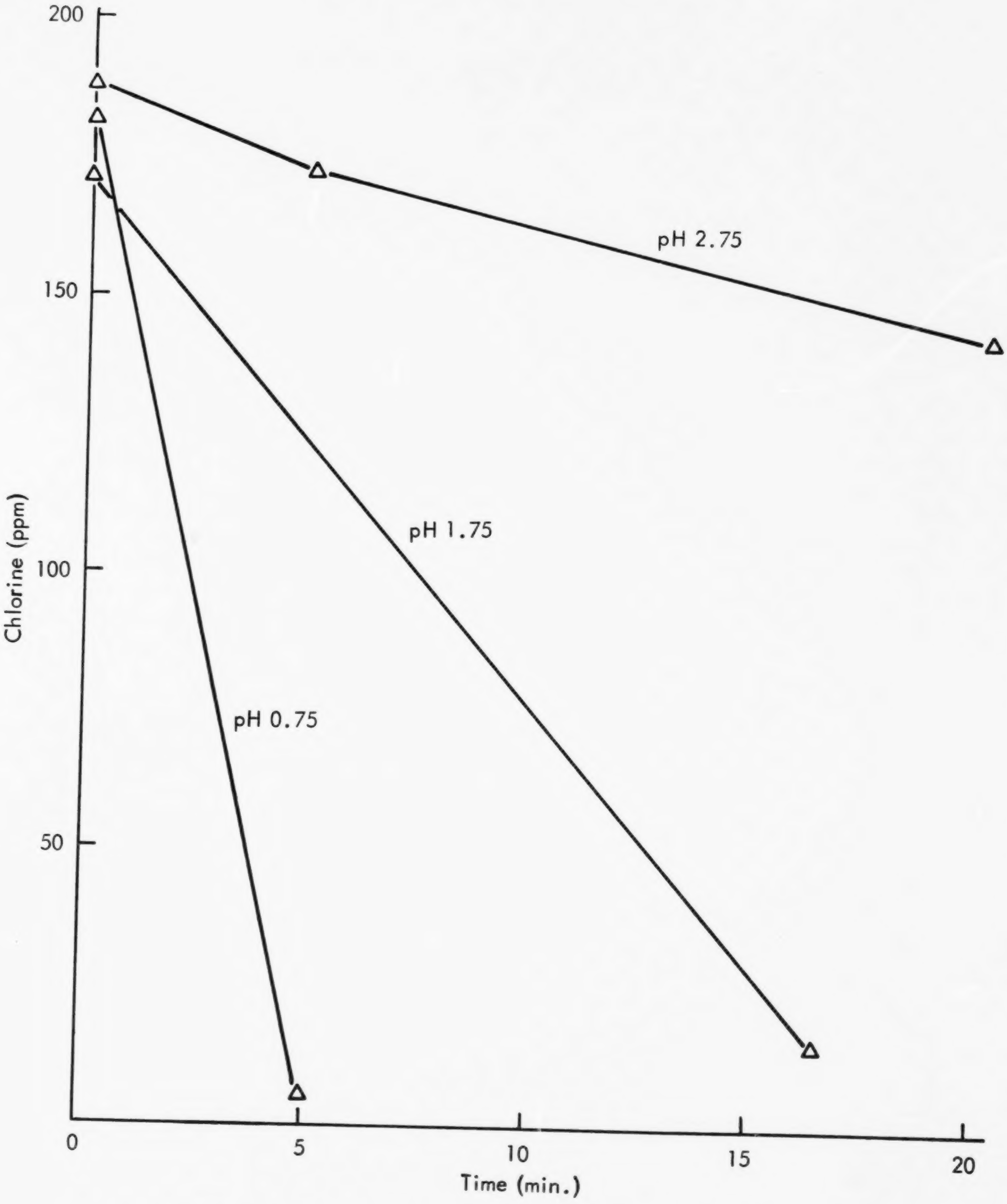

Figure 39 - Effect of pH on the Rate of Chlorine Removal From an Aqueous Solution During Nitrogen-Gas Purge

Since ammonia concentrations above 3-4 ppm could not be oxidized economically, effluents containing more than 4 ppm of ammonia nitrogen were further nitrified by means of the laboratory-scale, activated-sludge apparatus. (See p. 96.)

On arrival, the effluents were filtered through a cylindrical plug (1-1/4 in. diameter x 4 in.) of Pyrex, glass-wool, filtering fiber. This procedure removed 99% or more of the total suspended matter in the effluents. The filtered effluents were stored in a cold room (9°C) and were ordinarily used the same week that they were obtained. Each 5-gal. sample of effluent was filtered and analyzed on arrival for COD, TOC, ammonia, nitrate and (occasionally) nitrite. The COD and TOC determinations were repeated immediately before the oxidation experiments.

The Zinzer plant - The equipment used in this plant was manufactured by the Smith & Loveless Corporation. It has a capacity of 17,000 gal/day with a BOD loading of 34 lb/day. At the time it was sampled, this plant was loaded at a rate of 7,200 gal/day, and 15.3 lb. of BOD/day, during the summer months. During the remainder of the year, the load is increased to 15,855 gal/day and 38.38 lb. of BOD/day. The increased loading is caused by operation of an elementary school.

Some characteristics of the Zinzer plant are presented in Table XXV.

TABLE XXV

CHARACTERISTICS OF THE ZINZER PLANT

Model No. (Smith & Loveless)	12C17
Aeration tank	
Capacity (gal.)	17,000
Normal BOD capacity (lb/day)[a]	34
Blowers	
Recommended capacity (cfm)	72
Settling tank	
Total capacity (gal.)	3,949
Overflow rate (gal/sq. ft./day)	135

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[a] Based on 15 lb. of 5-day BOD/1,000 cu. ft. of aeration tank capacity.

The Nance plant - This plant is of the extended aeration type and was built in place. Only one of the two aeration tanks is presently in operation. The influent is aerated for 24 hr. at 1-2 ppm dissolved oxygen and passes to the settling tank where it is retained for 4 hr. Other characteristics of this plant are presented in Table XXVI.

TABLE XXVI

CHARACTERISTICS OF THE NANCE PLANT

Aeration Tanks	
Capacity, Each (gal.)	40,250
Retention Time (hr.)	24
Settling Tanks (2)	
Capacity, Each (gal.)	6,700
Retention Time (hr.)	4
Estimated BOD Load (lb/day)	68

The Randolph Corners plant - This plant serves 79 homes representing an inflow of 22,120 gal/day. The plant is very similar to the Zinzer plant, except that there are two units of 17,500-gal. capacity each.

The Gracemore plant - This plant uses a relatively new "Oxigest" design by Smith & Loveless. The process is more sophisticated than simple "Extended Aeration" and is a modification of conventional activated-sludge treatment known as "Contact Stabilization." A feature of this process is a re-aeration of the activated sludge.

The Gracemore plant is much larger than the other municipal sewage-treatment plants. During normal dry weather, the plant receives 195,300 gal/day. This figure increases to 500,000 gal/day during wet weather. The flow is divided, about half going to the Model R Oxigest facility and half going to an Imhoff-Tank, Trickling Filter. The Oxigest facility has a design, BOD-load capacity of 425 lb/day. During wet weather, the design flow is exceeded substantially.

Laboratory-Scale, Sewage-Treatment Apparatus

The apparatus was similar to the one described by Ludzack[13], and it incorporated most of the features of similar apparatus at the Cincinnati Water Research Laboratories (personal communications, E. F. Barth and C. E. Rhines). A photograph of the apparatus is presented in Figure 40.

The aerator compartment consists of a 9-liter, Pyrex, glass bottle with the bottom cut off and a 3/4-in. hole drilled in the side. The volume of this compartment, when filled to the overflow point, is 7.6 liters. The aerator compartment was placed in a specially designed hood equipped with Plexiglas doors and an exhaust fan which conducts air to an adjoining exhaust hood. Influent to the aerator flows from the bottom of a 5-gal. jug situated on top of the hood. Effluent from the aerator flows to a 5-gal. plastic carboy located under the hood.

The starting material used in this apparatus consisted of effluent obtained from a municipal plant (Gracemore). Control over the rate at which this material flows into the aerator compartment is maintained by an air bleed, through a needle valve (Nupro 4 M Fine Metering Valve), into the reservoir. The rate of flow was allowed to vary from about 4 to 8 liters/day.

Effluent Analyses

A summary of the characteristics of effluents obtained from various sewage treatment plants is presented in Table XXVII.

General Procedure

Filtered effluent (4.0 liters) was placed in the reactor, and samples of the untreated effluent were analyzed for total organic carbon (TOC), chemical oxygen demand (COD), ammonia and nitrate.

The pH of the effluent was adjusted to the desired value using concentrated sulfuric acid or 40% aqueous sodium hydroxide. Chlorine water was placed in the addition funnel, and an aliquot was taken for analysis. The volume of chlorine water in the funnel was adjusted to provide the desired initial chlorine concentration in the reactor. The chlorine water was added rapidly to the reactor, and the pH was readjusted--if necessary

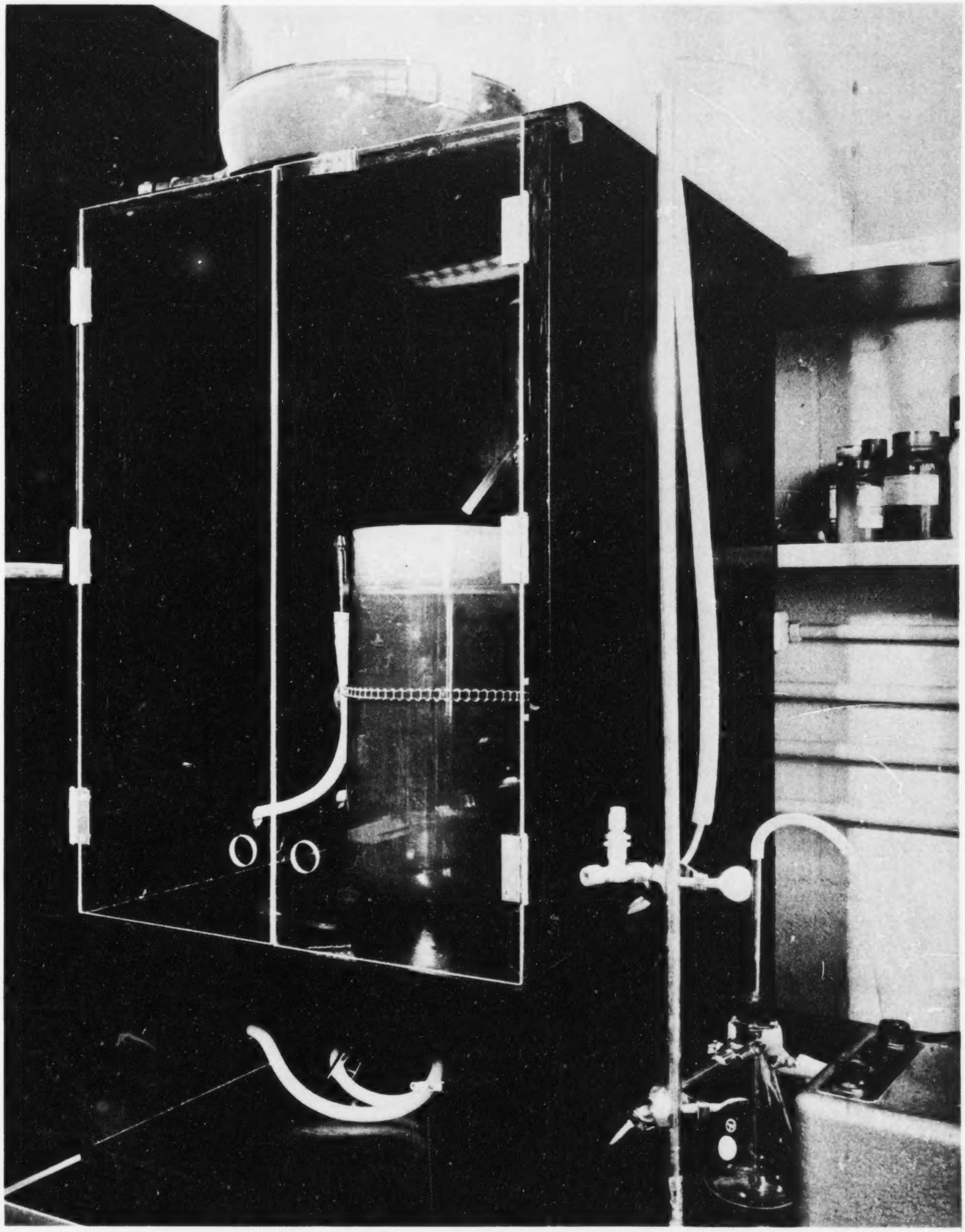

Figure 40 - Laboratory-Scale, Sewage-Treatment Apparatus

TABLE XXVII

ANALYSES OF EFFLUENTS USED IN THIS STUDY

Effluent*	Ammonia (ppm N)	Nitrate (ppm N)	COD (ppm)
Z-1	44.23	0.5	339.1
N-1	22.06	7.8	30.4
RC-1	7.8	1.8	35.4
G-1	3.8 (avg.)	1.67 (avg.)	29.4 (avg.)
G-2	13.9 (avg.)	0	49.7
G-3	30.5	-	-
G-4	30.2	-	-
G-5	16.9	-	-
RC-2	23.7, 25.7	-	-
G-5A	20	-	-
RC-3	21.8	-	-
G-6	32.0	-	-
S&L-1	1.8 (avg.)	11.0 (avg.)	35 (avg.)
S&L-3	2.1	11.5	24 (avg.)
S&L-5	0.9 (avg.)	10.6 (avg.)	22.0 (avg.)
S&L-6	1.6	13.4	18.9, 21.5
G-59C	14.38, 14.80	0.05	51.65, 43.43
MRI-428	2.2	15.8	31.2, 33.3
MRI-512	2.52	3.08	35.76, 34.54
MRI-516	1.33	11.50, 10.38	29.51, 29.66
G-528	19.98	0.15	207.3
MRI-61	4.33	24.00	23.74
S&L-619	22.6, 23.0	0.15, 0.15	26.53, 24.73
S&L-625	1.94, 2.60	3.74, 3.60	31.34, 31.41

---

* The first code letter, or letters, refer to the effluent source (G = Gracemore subdivision sewage treatment plant; Z = the Zinzer plant, N = the Nance plant; RC = Randolph Corners plant; S&L = Smith & Loveless Corporation, experimental plant, Lenexa, Kansas; MRI = effluent from laboratory-scale, sewage-treatment apparatus at Midwest Research Institute). The number after the code letter refers either to the sample number or to the date obtained (for example, 59 represents May 9th).

Usually, the chlorine-treated effluent was allowed to stand in the dark for about 10 min. During this time, the chlorine concentration was determined at various intervals; at the end of this period, samples were withdrawn for COD and TOC analyses.

The ultraviolet lamp, which was emitting at maximum intensity, was then placed within the immersion well. Samples for COD and TOC analyses were taken at about 5-min. intervals and were treated as before. The chlorine concentration was determined frequently during the irradiation period. In almost all the experiments, the pH of the reaction mixture was adjusted from time to time using 40% aqueous sodium hydroxide.

The acidified (pH 1) samples for COD analyses were dechlorinated by purging the sample with nitrogen gas until no chlorine could be detected by means of starch-iodide paper. The removal of chlorine by this method is facilitated by low pH values, and this step usually required 15-20 min. (longer periods of time were required when the effluent contained more than 4-5 ppm of ammonia). The TOC sample was taken separately, dechlorinated with excess solid sodium bisulfite, and similarly acidified.

Effect of Ultraviolet Radiation on Chlorine Water

The reactor was charged with tap water and chlorine water to provide 4,300 ml. of water containing about 200 ppm Cl_2. The pH was adjusted to the desired level (with concentrated HCl or 10% NaOH), the chlorine concentration was determined, and the UV lamp was turned on. Temperature of the contents of the flask was maintained by passing ice-water through the cooling jacket of the immersion well. The rates of decomposition at pH 5 and pH 10 are shown in Figure 20 (p. 44).

First Series of Wastewater Oxidation Experiments (Experiments 3-8)

The first series of six experiments was designed to investigate two levels of pH (5 and 10). Control experiments were run to determine the effect of chlorine in the dark and the effect of UV radiation in the absence of chlorine. The experimental design is shown in Table I (p. 6).

In this series of experiments, the UV lamp was placed in the reactor and turned on at the time indicated. In experiments to be performed in the dark, the reactor was covered with aluminum foil; and, of course, the lamp remained off.

The effluent used in the first series of experiments was obtained from the Gracemore sewage treatment plant (G-1). It was treated with sulfuric acid (4 ml/gal.) at the point of collection.

The analytical results for chlorine concentration, TOC and COD (plotted *vs*. time) are shown in Figures 3-8 (pp. 12-17).

In Experiments 3 and 4 (Figures 3 and 4), the final TOC and COD samples were taken at 27 and at 20 min., respectively. However, the chlorine was gone after about 17 min. and 8 min., respectively. Because of this inopportune sampling time, oxidation rates at pH 5 and pH 10 could not validly be compared with these data.

Second Series of Effluent Oxidation Experiments (Experiments 39-47)

The effluent used in this series was obtained from the Smith & Loveless,experimental,sewage-treatment plant (S&L-5). The experimental design is presented in Table VI (p. 20). The COD and TOC samples were taken simultaneously; the samples were acidified (pH 1) with sulfuric acid and then purged with nitrogen until no chlorine could be detected using starch-iodide paper. Part of each sample was sent to Cincinnati for TOC determination, and the remainder was analyzed for COD.

Experiment 39: High chlorine (175 ppm), pH 8.5, 15 min. irradiation

Time (min.)	Sample	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	39A	--	20.7, 20.9	10.2
0	Cl_2 added*	171	--	--
2.2	--	119.7	--	--
5.0	--	166.0	--	--
9.5	--	185.5	--	--
9.9	39B	--	13.6, 14.7	8.8
21.2	Lamp inserted	--	--	--
26.2	--	43.5	--	--
31.2	--	12.0	--	--
36.2	39C	6.9	9.1, 11.8	21.5

---

* 290 ml. chlorine water (containing 2,530 ppm chlorine).

Experiment 40: Low chlorine (102 ppm), pH 8.5, 10 min. irradiation

Time (min.)	Sample	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	40A	--	24.1, 23.3	9.6
0	Cl_2 added*	102	--	--
3.9	--	93.1	--	--
6.5	--	98.4	--	--
9.2	--	93.9	--	--
10.0	40B	--	16.6, 13.7	6.0
10.5	Lamp inserted	--	--	--
15.5	--	21.8	--	--
20.5	40C	6.9	12.9	21.0

---

* 175 ml. chlorine water (containing 2,430 ppm chlorine).

Experiment 41: No chlorine, 10 and 15 min. irradiation

Time (min.)	Sample	pH	COD (ppm)	TOC (ppm)
0	Lamp inserted	7.5	20.4, 21.2	9.6
10.4	41A	7.4	24.8, 18.1	8.6
15.8	41B	7.4	18.1	7.8

Experiment 42: Low chlorine (102 ppm), pH 8.5, 15 min. irradiation

Time (min.)	Sample	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	42A	--	19.7, 18.9	12.4
0	Cl_2 added*	102	--	--
2.3	--	92.7	--	--
5.0	--	99.6	--	--
9.2	--	98.5	--	--
9.8	42B	--	19.4, 18.1	11.4
10.6	Lamp inserted	--	--	--
15.7	--	25.9	--	--
20.6	--	2.3	--	--
25.6	42C	0.0	11.9, 11.9	7.8

---

* 180 ml. chlorine water (containing 2,360 ppm chlorine).

Experiment 43: High chlorine (175 ppm), pH 6.5, 10 min. irradiation

Time (min.)	Sample	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	43A	--	20.6, 17.8	8.6
0	Cl_2 added*	178.0	--	--
2.1	--	160.3	--	--
5.1	--	171.3	--	--
9.2	--	171.7	--	--
10.2	43B	--	14.0, 17.8	8.2
12.9	Lamp inserted	--	--	--
17.9	--	71.0	--	--
22.9	43C	10.3	8.7, 8.4	6.0

---

* 325 ml. chlorine water (containing 2,370 ppm chlorine).

Experiment 44: High chlorine (175 ppm), pH 6.5, 15 min. irradiation

Time (min.)	Sample	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	44A	--	17.5, 20.9	28.0
0	Cl_2 added*	178	--	--
1.5	--	170.2	--	--
5.2	--	176.3	--	--
9.2	--	176.9	--	--
9.8	44B	--	18.2, 18.7	8.4
10.8	Lamp inserted	--	--	--
15.8	--	60.7	--	--
20.8	--	6.2	--	--
25.8	44C	0.6	6.4, 8.0	4.6

---

* 325 ml. chlorine water (containing 2,370 ppm chlorine).

Experiment 45: Low chlorine (102 ppm), pH 6.5, 15 min. irradiation

Time (min.)	Sample	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	45A	--	22.8, 21.8	9.0
0	Cl_2 added*	104	--	--
2.1	--	93.9	--	--
5.3	--	97.0	--	--
9.0	--	97.0	--	--
9.8	45B	--	18.7, 19.9	9.4
10.2	Lamp inserted	--	--	--
16.5	--	5.7	--	--
20.1	--	0.2	--	--
25.2	45C	0.0	4.6, 8.7	9.8

---

* 190 ml. chlorine water (containing 2,290 ppm chlorine).

Experiment 46: Low chlorine (102 ppm), pH 6.5, 10 min. irradiation

Time (min.)	Sample	pH	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	46A	7.7	--	22.2	7.8
0	Cl_2 added*	--	102	--	--
2.5	--	--	88.9	--	--
5.2	--	--	91.6	--	--
7.9	--	6.4	--	--	--
8.8	--	--	95.0	--	--
10.2	46B	--	--	15.2, 14.4	8.4
10.6	Lamp inserted	--	--	--	--
11.0	--	6.3	--	--	--
15.7	--	--	28.6	--	--
20.6	46C	6.2	0.6	7.1, 5.6	6.2

---

* 200 ml. chlorine water (containing 2,136 ppm chlorine).

Experiment 47: High chlorine, (175 ppm), pH 8.5, 10 min. irradiation

Time (min.)	Sample	pH	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	47A	7.7	--	20.2	10.0
0	Cl_2 added*	--	174	--	--
2.4	--	--	162.3	--	--
4.6	--	8.5	--	--	--
4.9	--	--	168.3	--	--
8.9	--	--	168.9	--	--
9.8	47B	--	--	12.4, 13.7	7.2
10.1	--	8.85	--	--	--
10.4	Lamp inserted	--	--	--	--
15.2	--	--	45.8	--	--
18.8	--	8.25	--	--	--
20.4	47C	--	2.1	8.2, 9.0	6.8

---

* 345 ml. chlorine water (containing 2,191 ppm chlorine).

Third Series of Effluent Oxidation Experiments (Experiments 48-50, 52-54, and 77 and 78)

A major difference in procedure was followed in this series; TOC and COD samples were taken separately. The TOC samples (30 ml.) were immediately treated with excess sodium bisulfite and acidified with concentrated sulfuric acid (4 drops/30 ml. sample) to pH 1. The COD sample (120 ml.) was acidified, as before, to pH 1 and purged with a stream of nitrogen until no chlorine could be detected using starch-iodide paper. In a number of these experiments, a second addition of chlorine approximately equal to the first was made after most of the original chlorine had been consumed.

Experiment 48: pH 3.0, 26 min. irradiation, two-stage chlorine addition

Time (min.)	Sample	pH	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	48A*	--	--	19.3	--
0	48-1*	--	--	--	7.8
0	Cl_2 added**	--	127	--	--
2.2	--	--	112.8	--	--
3.6	--	3.6	--	--	--
5.1	--	--	119.1	--	--
9.6	--	--	118.5	--	--
9.7	48-2	--	--	--	7.0
10.2	48B	--	--	15.0, 15.0	--
11.2	Lamp inserted	--	--	--	--
15.6	--	2.7	--	--	--
15.9	--	--	50.2	--	--
16.1	48-3	--	--	--	7.0
16.9	48C	--	--	12.2, 13.5	--
20.9	--	9.0	--	--	--
21.0	48-4	--	--	--	6.4
21.5	48D	--	--	13.5, 10.7	--
25.8	48-5	--	< 0.5	--	6.4
26.5	48E	--	--	8.8, 10.7	--
27.4	Cl_2 added**	--	--	--	--
29.2	--	--	91.6	--	--
29.5	--	3.05	--	--	--
32.1	--	--	51.0	--	--
37.4	48F	--	--	4.2***	--
37.4	48-6	2.2	16.6	--	6.0***

---

* Smith and Loveless, S&L-6-A.

** 275 ml. chlorine water (containing 1,957 ppm chlorine).

*** Adjusting for the second addition of chlorine, the following values are obtained: 48-F, COD = 4.56; 48-6, TOC = 6.5.

Experiment 49: pH 6.5, 25 min. irradiation two-stage chlorine addition

Time (min.)	Sample	pH	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	49A*	7.6	--	27.19	--
0	49-1	--	--	--	8.0
0	Cl_2 added**	--	125	--	--
0.8	--	6.9	--	--	--
2.0	--	--	109.9	--	--
4.8	--	--	127.6	--	--
9.2	--	--	117.7	--	--
9.3	49-2	--	--	--	7.4
9.8	49B	--	--	24.72, 25.52	--
10.6	Lamp inserted	--	--	--	--
11.1	--	6.5	--	--	--
13.2	--	5.9	--	--	--
15.6	--	--	40.0	--	--
15.8	49-3	--	--	--	4.6
16.2	49C	--	--	13.55, 12.44	--
18.2	--	5.2	--	--	--
20.4	--	--	2.3	--	--
20.7	49-4	--	--	--	3.4
21.1	49D	--	--	6.40, 6.60	--
23.3	Cl_2 added**	--	--	--	--
23.9	--	4.35	--	--	--
25.3	--	--	51.9	--	--
27.2	49-5	--	--	--	2.2***
27.7	49E	--	--	4.64, 4.75***	--
28.2	--	--	30.0	--	--
36.8	49F	--	--	0,0	--
36.8	49-6	6.6	4.5	--	1.8***

---

* Smith and Loveless, S&L-6-A.

** 300 ml. chlorine water (containing 1,790 ppm chlorine).

*** Adjusting for the dilution produced by the second addition of chlorine, the following values are obtained: 49E, COD = 5.1; 49-5, TOC = 2.4; 49-6, TOC = 1.96.

Experiment 50: pH 6.5, 15 min. irradiation

Time (min.)	Sample	pH	Chlorine (ppm)	COD (ppm)	TOC (ppm)
0	50A*	--	--	29.75	--
0	50-1	7.5	--	--	12
0	Cl_2 added**	--	168	--	--
1.1	--	4.8	--	--	--
1.9	--	--	157.5	--	--
4.3	--	4.8	--	--	--
4.8	--	5.1	162.0	--	--
5.3	--	7.8	--	--	--
9.3	--	6.7	161.4	--	--
10.4	50-2	--	--	--	10
10.5	50B	--	--	24.58, 26.71	--
11.0	Lamp inserted	6.4	--	--	--
14.0	--	--	75.9	--	--
16.1	50-3	--	--	--	5.4
16.3	50C	--	--	6.44, 6.00	--
17.0	--	--	13.6	--	--
19.4	--	4.0	--	--	--
20.9	--	5.9	2.1	--	--
22.1	50-4	5.9	--	--	3.4
22.2	50D	--	--	3.08, 2.92	--
25.7	--	--	0.5	--	--
26.2	50E	--	--	2.92	--
26.2	50-5	--	--	--	3.2

---

* Laboratory-produced effluent, MRI-428.

** 505 ml. chlorine water (containing 1,493 ppm chlorine).

Experiments 52-54 - Three experiments were designed to investigate the rate and extent of UV-catalyzed chlorine oxidation at pH 3, pH 5 and pH 10. The effluent (MRI 512) used in these experiments contained 33.8 mg/liter COD, 13.2 mg/liter TOC, 2.5 mg/liter of ammonia nitrogen and 4.0 mg/liter nitrate nitrogen (average values). In each experiment, the effluent was treated with chlorine water to provide an initial chlorine concentration of about 200 ppm. This concentration represents a 33% excess over the theoretical amount of chlorine required to oxidize all of the organic material to CO_2 and H_2O.

The experiments were performed at room temperature and were identical, except that each was performed at a different pH (pH 3, pH 5 and pH 10). The experimental results are shown in Figures 12-14 (pp. 38-40). The COD and TOC data are presented graphically in Figures 15-16 (p. 41).

Experiment 77, the effect of nitrate concentration - In Experiment 77, 20 ppm of nitrate nitrogen (as potassium nitrate) was added to an effluent prior to treatment with chlorine. The effluent (S&L 624A) was the same as the one used in Experiment 75 (Figure 22). The results of the experiment (Experiment 77) with the nitrate-containing effluent are shown in Figure 21 (p. 45).

Experiment 78, the effect of chlorine concentration; Effluent S&L 624A, pH 5, continuous addition of chlorine - In this experiment, the chlorine water was not added all at once, but was added gradually during the irradiation period. The results are shown in Figure 19 (p. 43).

The effect of temperature on the UV-catalyzed chlorine oxidation of effluents - Two effluent oxidation experiments (Experiments 58 and 59) were performed in exactly the same manner; except that, in one, the temperature was held near 5°C (41°F) and, in theother, the temperature was held near 25°C (77°F). The results are shown in Figures 23 and 24 (pp. 47-48).

Extent of Organic Oxidation Produced by Chlorine in the Dark

A summary of the extent of COD and TOC decreases which occurred during a 10-min. period of chlorination in the dark is presented in Table XXVIII. In each of these experiments, the TOC sample was not submitted to the nitrogen purge; instead, it was dechlorinated by acidification to pH 1 with sulfuric acid, followed by treatment with excess sodium bisulfite.

TABLE XXVIII

EXTENT OF COD AND TOC ELIMINATION PRODUCED BY A 10-MIN. PERIOD OF CHLORINATION IN THE DARK

Experiment No.	Effluent[a]	pH	COD Elimination (%)	TOC Elimination (%)
48	S&L-6	3.0	16.7	4.0
49	S&L-6	6.5	0.8	0.5
50	MRI-428	6.5	3.3	6.6[b]
52	MRI-512	3.0	11.8	0
53	MRI-512	10	12.1	6.7
54	MRI-512	5	11.3	2.5
55	MRI-516	5	14.7	4.0
56	MRI-516	5	15.4	21.5[b]
57	MRI-516	10	20.0	15.3
58	MRI-525	5	14.4	6.5
59	MRI-525	5	16.4	[c]
75	S&L-624	5	2.0	28.3[b]
77	S&L-624	5	16.4	11.7
Average			11.94	5.68

---

[a] The significance of the effluent designation is explained at the bottom of Table XXVII (p. 98).

[b] These TOC results are probably in error, because the extent of the TOC elimination cannot be greater than the extent of COD elimination (These TOC results were not included in the average).

[c] In this experiment, the TOC analysis indicated an increase in TOC.

Extent of COD and TOC Elimination Produced by Irradiation at pH 5

The following table (Table XXIX) presents a summary of the experiments performed at pH 5 in which the COD and TOC samples were taken separately. The average amount of COD and TOC eliminated was calculated, and these values are plotted *vs*. time in Figures 17 and 18 (p. 42).

TABLE XXIX

EXTENT OF COD AND TOC ELIMINATION AT pH 5

Experiment No.	Effluent No.	Extent of COD Elimination (%)[a]			Extent of TOC Elimination (%)[a]		
		5 min.	10 min.	15 min.	5 min.	10 min.	15 min.
54	MRI-512	70	80	100[b]	35	60	81[b]
56	MRI-516	84	--	--	50	--	--
58[c]	MRI-525	69	90	100[b]	32	53	--
59[c]	MRI-525	80	100	100	30	55	--
75	S&L-624	60	67	88[b]	43	--	70[b]
77[d]	S&L-624	51	66	90[b]	27	50	80[b]
78[e]	S&L-624	52	71	89	15	44	70
Average[f]		66.6	79.0	94.5	33.1	52.4	75.3

---

[a] If the actual time periods between analytical determinations were not exactly 5, 10 or 15 min., the percentage figures were adjusted proportionately.

[b] At the time these determinations were made, a second addition of chlorine had been made.

[c] Experiment 58 was run at 5°C; Experiment 59 was run at 25°C.

[d] In Experiment 77, 20 ppm of nitrate nitrogen was added to reaction mixture.

[e] In Experiment 78, the chlorine was added continuously during the irradiation period.

[f] The average figures are plotted *vs*. time in Figures 17 and 18 (p. 42).

Ultraviolet-Catalyzed Chlorine Oxidation of High-Ammonia Effluents (Experiments 20, 21, 23, 27-29, 30, 75 and 76)

These experiments were performed in accordance with the general procedure described earlier. (Samples were dechlorinated by acidification and a nitrogen purge prior to ammonia, nitrate and COD analyses.) However, in some cases (as indicated), the UV lamp was not turned on and allowed to warm up prior to insertion into the reactor. The experimental details are summarized below.

Experiment 20: Effluent G-2, 180 ppm chlorine, pH 5, 13 min. irradiation

Time (min.)	Sample	pH	Chlorine (ppm)	Ammonia (ppm N)	Nitrate (ppm N)	COD (ppm)
0	20A	7.1	0	15.1*	0	51.6
0	Cl_2 added	--	180	--	--	--
1.3	--	9.2	116	--	--	--
8.5	Lamp on	--	--	--	--	--
11.9	--	6.4	105	--	--	--
15.3	20B	--	--	3.5	3.6	--
18.2	--	--	6.0	--	--	--
19.3	--	4.75	--	--	--	--
20.3	--	--	2.0	--	--	--
21.3	20C	4.7	--	4.3	3.5	28.1

---

* Solution was turbid.

Experiment 21: Effluent G-2, 170 ppm chlorine, pH 10, 8.5 min. irradiation

Time (min.)	Sample	pH	Chlorine (ppm)	Ammonia (ppm N)	Nitrate (ppm N)	COD (ppm)
0	21A	7.05	0	12.7*	0	47.7
0	Cl_2 added	--	170	--	--	--
1.3	--	10.25	93	--	--	--
10.5	Lamp on	--	--	--	--	--
10.8	--	--	92	--	--	--
12.0	--	9.4	--	--	--	--
13.1	--	--	88	--	--	--
15.4	21B	--	--	1.6	2.5	--
17.2	--	--	9.0	--	--	--
19.0	21C	--	0.6	2.5	3.4	22.3

---

* Solution was turbid.

Experiment 23: Effluent RC-3, 389 ppm chlorine, 15 min. in dark, 15 min. irradiation

Time (min.)	Sample	pH	Chlorine (ppm)	Ammonia (ppm N)	Nitrate (ppm N)	COD (ppm)
0	23A	7.4	0	21.4	1.65	159
0	Cl_2 added	--	389	--	--	--
2.0	--	4.8	275	--	--	--
6.5	--	4.7	268	--	--	--
10.7	--	--	263	--	--	--
14.2	23B	--	262	18.5	1.80	130
15.0	Lamp inserted	--	--	--	--	--
15.9	--	--	--	--	--	--
18.2	--	3.9	--	--	--	--
28.6	--	2.4	--	--	--	--
30.0	23C	--	43	5.0	6.80	112

Experiment 27: Effluent RC-3, 375 ppm chlorine, pH 5, 15 min. in dark, 15 min. irradiation

Time (min.)	Sample	pH	Chlorine (ppm)	Ammonia (ppm N)	Nitrate (ppm N)	COD (ppm)
0	27A	7.2	0	20.3	2.1	156
0	Cl_2 added	--	375	--	--	--
1.6	--	6.0	--	--	--	--
4.5	--	--	169.5	--	--	--
9.5	--	5.5	225.6	--	--	--
13.3	--	--	221.3	--	--	--
15.0	27B	--	--	20.8	1.8	134.6
16.7	Lamp inserted	--	--	--	--	--
18.3	--	10.6*	--	--	--	--
21.8	--	--	53.8	--	--	--
27.8	--	--	11.5	--	--	--
31.7	27C	--	9.2	3.2	7.1	123.7

---

* Occasionally, an excess of sodium hydroxide was inadvertantly added. The pH was adjusted downward as soon as possible using concentrated sulfuric acid.

Experiment 28: Effluent RC-3, 373 ppm chlorine (Added gradually), 60 min. in dark, pH maintained above 6.5

Time (min.)	Sample	pH	Chlorine (ppm)	Ammonia (ppm N)
0	28A	7.2	0	20.6
0	Start Cl_2 addition	--	373	--
16.8	--	6.8	49.2	--
26.9	--	--	75.6	--
37.9	--	--	60.7	--
45.4	Complete Cl_2 addition	--	--	--
46.7	--	--	99.6	--
60.0	28B	6.4	130.5	2.9

Experiment 29: Effluent RC-3, 375 ppm chlorine (Added all at once), 60 min. in dark, pH maintained above 6.5

Time (min.)	Sample	pH	Chlorine (ppm)	Ammonia (ppm N)
0	29A	7.2	0	22.4
0	Cl_2 added	--	375	--
8.2	--	6.9	151.1	--
12.6	--	6.9	162.6	--
25.6	--	6.85	161.4	--
38.0	--	6.75	155.7	--
60.0	29B	6.7	140.8	6.7

Experiment 30: Effluent RC-3, 374 ppm chlorine (Added gradually), 60 min. in dark, 15-min. irradiation, pH 6.5

Time (min.)	Sample	pH	Chlorine (ppm)	Ammonia (ppm N)	Nitrate (ppm N)	COD (ppm)
0	30A	7.2	--	22.9	2.0	126
0	Start Cl_2 addition	--	--	--	--	--
7.8	--	6.8	--	--	--	--
12.3	--	6.6	--	--	--	--
16.4	--	--	41.2	--	--	--
38.7	--	6.55	64.1	--	--	--
43.1	Complete Cl_2 addition	--	--	--	--	--
58.6	--	--	97.3	--	--	--
60.8	30B	--	--	3.3	2.6	103
62.1	Lamp inserted	--	--	--	--	--
77.1	--	6.9	21.8	4.2	3.1	92

Experiments 75 and 76: The effect of adding ammonia to a highly nitrified effluent - The effluent used in Experiment 75 was low in ammonia content (1.9 ppm ammonia nitrogen). Experiment 76 was performed using the same effluent to which 23 ppm ammonia nitrogen (as ammonium chloride) was added. The results of these experiments are shown in Figures 22 and 25 (pp. 46 and 53).

Ultraviolet-Catalyzed Chlorine Oxidation of Ammonia

Experiments 13, 15, 17 and 26 were performed in accordance with the general procedure, except that a solution of ammonium chloride was used in place of an effluent. In some cases, as indicated, the lamp was not turned on and allowed to warm up prior to insertion into the reactor. Except as indicated, samples for ammonia and nitrate analyses were dechlorinated by acidification to pH 1 with sulfuric acid, followed by nitrogen purge until no chlorine could be detected with starch-iodide paper.

Experiment 13: Ammonium chloride, 148 ppm chlorine, pH 5, 15 min. irradiation

Time (min.)	Sample	Chlorine (ppm)	Ammonia (ppm N)	Nitrate (ppm N)
0	13A	0.0	12.8	--
0	Cl_2 added	148.0	--	--
2.7	--	43.0	--	--
3.7	Lamp on	--	0.2	0.8
5.3	13B	--	--	--
9.8	--	12.5	--	--
13.8	13C	--	0.1	2.2
14.8	--	3.5	--	--
18.3	13D	--	--	2.0

Experiment 15: Ammonium chloride, no chlorine, pH 5, 182 min. irradiation

Time (min.)	Sample	Ammonia (ppm)	Nitrate (ppm)
0	15B	12.7	0.50
93	15C	13.0	--
182	15D	10.8	0.05

Experiment 17: Ammonium chloride, 408 ppm chlorine, pH 5, 6 days in dark, followed by 32 min. irradiation - This experiment was performed in the dark using aluminum foil to cover the entire reactor. After 6 days, the lamp was turned on.

Time (min.)	Sample	Chlorine (ppm)	Ammonia (ppm N)	Nitrate (ppm N)
0	17A	0	13.5	0.02
0	Cl_2 added	408	--	--
5.7	17B	--	0.0	0.22
8.5	--	348	--	--
44.1	--	293	--	--
0 (4 days later)	17C	229	1.6	4.0
0	Lamp on	--	--	--
4.3	--	213	--	--
9.6	--	138	--	--
17.5	--	48	--	--
20.0	--	32	--	--
31.0	--	9.5	--	--
32.0	17D	--	0.0	9.0
		115		

Experiment 26: Ammonium chloride, 304 ppm chlorine, 15 min. in dark, 15 min. irradiation

Time (min.)	Sample	pH	Chlorine (ppm)	Ammonia (ppm N)	Nitrate (ppm N)
0	26A	6.4	0	28.8	0
0	Cl_2 added	--	304	--	--
1.5	--	5.6	--	--	--
2.3	--	--	137.4	--	--
4.3	--	5.3	--	--	--
4.8	--	--	171.8	--	--
8.6	--	--	177.5	--	--
11.7	--	4.9	--	--	--
15.0	26B*	--	--	24.4	0.25
	26C**	--	--	9.1	0.05
16.9	Lamp inserted	--	--	--	--
24.2	--	2.5	--	--	--
30.0	26D*	--	36.8	4.6	6.35
30.0	26E**	--	--	4.0	6.95

---

* Samples 26B and 26D (150 ml.) were acidified with concentrated sulfuric acid (1 ml.) and treated with about 0.3 g. of sodium bisulfite (Reagent grade, Merck). The solutions were then aerated until no odor of SO_2 could be detected. Prior to ammonia analysis, the solution was adjusted to pH 10 with sodium hydroxide (40% NaOH, followed by 5% NaOH).

** Samples 26C and 26E (150 ml.) were acidified with concentrated sulfuric acid (1 ml.), and nitrogen was bubbled through the resulting solutions until no trace (or only a faint trace) of chlorine could be detected by starch-iodide paper.

Comparison of UV Radiation Sources

Using the low-pressure, mercury-arc lamp, effluent oxidation experiments were conducted at pH 5 and at pH 10; and the same effluent was treated in the same manner using the high-pressure UV source. The results of these experiments (Experiments 55-57) are presented in Figures 27-29 (pp. 64-66).

UV-Catalyzed Chlorine Oxidation of Pure Compounds (Experiments 60-63, 68-70)

Aqueous solutions of eight pure compounds were subjected to conditions approximating those of the effluent oxidation experiments.

Only the rate and extent of compound destruction were measured, usually by TOC determinations or ultraviolet spectra analyses; and no attempt was made to determine the number or kind of products formed. In all of these experiments, the pH was maintained near 5.0. The results of these experiments are shown in Figures 30-35 (pp. 71-76).

Investigation of the Effect of UV Radiation, Plus Other Oxidizing Agents

Treatment of wastewater with oxygen and UV radiation - In experiment 80, pure oxygen gas was continuously bubbled through an effluent while the reaction mixture was irradiated. (No adjustment of pH was made prior to, or during, the experiment.) In Experiment 79, nitrogen gas was bubbled through another sample of the same effluent while the solution was irradiated. The results of these experiments are shown below:

Experiment 79: Effluent S&L-624B, nitrogen purge, no chlorine

Time (min.)	Sample	pH	TOC (ppm)
0	79A	7.25	12.8
0	Lamp inserted; N_2 flow started		
5.1	79C	7.40	12.0
10.0	79D	7.55	11.0
15.1	79E	7.70	10.0
20.0	79F	7.81	--

Experiment 80: Effluent S&L-624B, oxygen purge, no chlorine, 19.9 min. irradiation

Time (min.)	Sample	pH	TOC (ppm)
0	80A	7.32	10.2
0	Lamp inserted; O_2 flow started		
5.1	80C	7.50	11.0
10.1	80D	7.60	10.0
14.9	80E	7.75	10.0
19.9	80F	7.90	10.2

Treatment of wastewater with hydrogen peroxide and UV radiation - The same effluent used in the above series of experiments was treated in the dark with hydrogen peroxide in excess of the amount required to oxidize all of the organic material in the effluent to CO_2. The reaction mixture was kept in the dark for 30 min. and was then irradiated for 30 min. The results of this experiment are shown in Figure 36 (p. 79).

Ultraviolet Absorbance of Treated and Untreated Wastewater Samples

Ultraviolet spectra of a number of treated and untreated wastewater samples were obtained. A description of the samples is presented in Table XXX, and the absorbance values at wavelengths between 230 mμ and 340 mμ are presented in Table XXXI.

The results of these determinations clearly show that large decreases in absorbance are produced by UV-catalyzed chlorine oxidation. There are correspondingly large increases in the "Effective Depth of Penetration" (EDP), a term which is defined on p. 85.

The EDP is equal to the reciprocal of the absorbance; thus, an absorbance of zero is equivalent to an EDP of infinity, an absorbance of 0.01 is equivalent to an EDP of 100 cm., and an absorbance of 1.0 indicates an EDP of 1 cm.

The data were obtained using a Beckman DK-2 spectrophotometer and a cell of 1-cm. thickness. The indicated absorbances of some of the treated samples are very nearly zero. Determination of more exact values would require use of much longer cells.

Note that decreases in absorbance are produced more rapidly than decreases in COD or TOC. For example, with effluent MRI 516, a 31.5% decrease in COD (from the pure effluent to sample 55E) was accompanied by a 51% decrease in absorbance at 260 mμ

TABLE XXX

DESCRIPTION OF TREATED AND UNTREATED WASTEWATER SAMPLES FOR WHICH UV ABSORBANCE DATA ARE AVAILABLE

Effluent	Sample No.*	COD (ppm)	TOC (ppm)	NH_3 (ppm N)	Nitrate (ppm N)	Treatment
MRI 428	(50A)	29.75	12.0	2.3	15.8	None
MRI 428	(50F)	2.92	3.2	-	-	168 ppm Cl_2, pH 6.5, 13 min. in the dark, 15 min. irrad. (Expt. 50, p. 37)
MRI 512		35.6	12.1	2.52	3.1	None
MRI 512	(54G)	0	1.6	-	-	200 ppm Cl_2, pH 5, 13 min. in the dark, 28 min. irrad. (addn'l 200 ppm Cl_2 added after 13 min. irrad.) (Expt. 54, p. 40)
MRI 516		29.6	11.0	1.3	10.7	None
MRI 516	(55E)	9.3	7.0	-	-	210 ppm Cl_2, pH 5, 10 min. in the dark, 30 min. irrad. with low pressure source (Expt. 55, p. 64)
MRI 516	(56E)	0	3.2	-	-	212 ppm Cl_2, pH 5, 11 min. in the dark, 12 min. irrad. (Expt. 56, p. 65)

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* The sample number is the experiment number, plus a letter designating the appropriate sample. This numbering system is identical to that used elsewhere in the report.

TABLE XXXI

ULTRAVIOLET ABSORBANCE OF TREATED AND UNTREATED WASTEWATER SAMPLES

Sample		Absorbance at Indicated Wavelength											
	Wavelength (mμ) ⟶	230	240	250	260	270	280	290	300	310	320	330	340
MRI 428 (50A)	Untreated	>1.100	0.322	0.200	0.187	0.180	0.162	0.140	0.123	0.108	0.092	0.080	0.070
" (50F)	Chlorinated*	0.720	0.080	0	0	0.002	0.007	0.012	0.017	0.017	0.017	0.016	0.017
MRI 512	Untreated	0.600	0.310	0.245	0.232	0.218	0.190	0.160	0.133	0.115	0.100	0.090	0.075
" (54G)	Chlorinated*	0.235	0	0	0	0	0	0	0	0	0	0	0
MRI 516	Untreated	0.940	0.300	0.200	0.192	0.180	0.160	0.135	0.115	0.100	0.087	0.078	0.068
" (55E)	Chlorinated*	0.760	0.240	0.140	0.095	0.075	0.070	0.072	0.070	0.064	0.055	0.047	0.040
" (56)	Chlorinated*	0.580	0.060	0	0	0	0	0	0	0	0	0	0

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* Details of the chlorine treatment are presented in TABLE XXX.

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